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PROPERTIES AND BIBLIOGRAPHY OF GaSe

WRIGHT LABORATORY

NILS C. FERNELIUS

FEBRUARY 1994

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MATERIALS DIRECTORATE
WRIGHT LABORATORY
AIR FORCE MATERIAL COMMAND
WRIGHT-PATTERSON AFB OH 45433-7734

NOTICE

THIS TECHNICAL REPORT HAS BEEN REVIEWED AND IS APPROVED FOR PUBLICATION.

Nils C. Fernelius

NILS C. FERNELIUS, Research Physicist
Electronic & Optical Mat'ls Branch
Electromagnetic Mat'ls & Surv. Div.

Robert L. Denison

ROBERT L. DENISON, Chief
Electronic & Optical Mat'ls Branch
Electromagnetic Mat'ls & Surv. Div.

William R Woody

WILLIAM R. WOODY, Chief
Electromagnetic Mat'ls & Surv. Div.
Materials Directorate

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13. ABSTRACT *(Maximum 200 words)*

GaAs appears to be a possible candidate material for optical frequency conversion devices in the near to far infrared (2-18 um wavelength). Various properties of this material are important to researchers and systems designers to assess the utility of the material and to develop applications. A search of the published literature amassed over 600 articles. An attempt was made to organize this material by growth, structural and mechanical, thermal, electrical and optical properties. More effort was made to condense thermal and optical properties along with accounts of nonlinear optical (NLO) usages. A summary of the good and bad properties for NLO applications is given.

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The author thanks the staff of the Wright Laboratory Technical Library for help in tracking down copies of many of the more obscure references. Much of the work on GaSe was done in the Soviet Union. The most active centers were Institutes of the Academy of Sciences in Baku (Azerbaidzhan), Leningrad, Moscow and Kiev. Much information on Soviet work was gathered from the National Aerospace Intelligence Center. Mr. Bruce Armstrong, NAIC/TATD, obtained and had translated a number of Russian articles.

PROPERTIES AND BIBLIOGRAPHY OF GaSe

Nils C. Fernelius
Materials Directorate
Wright Laboratory
Wright-Patterson AFB, Ohio 45433

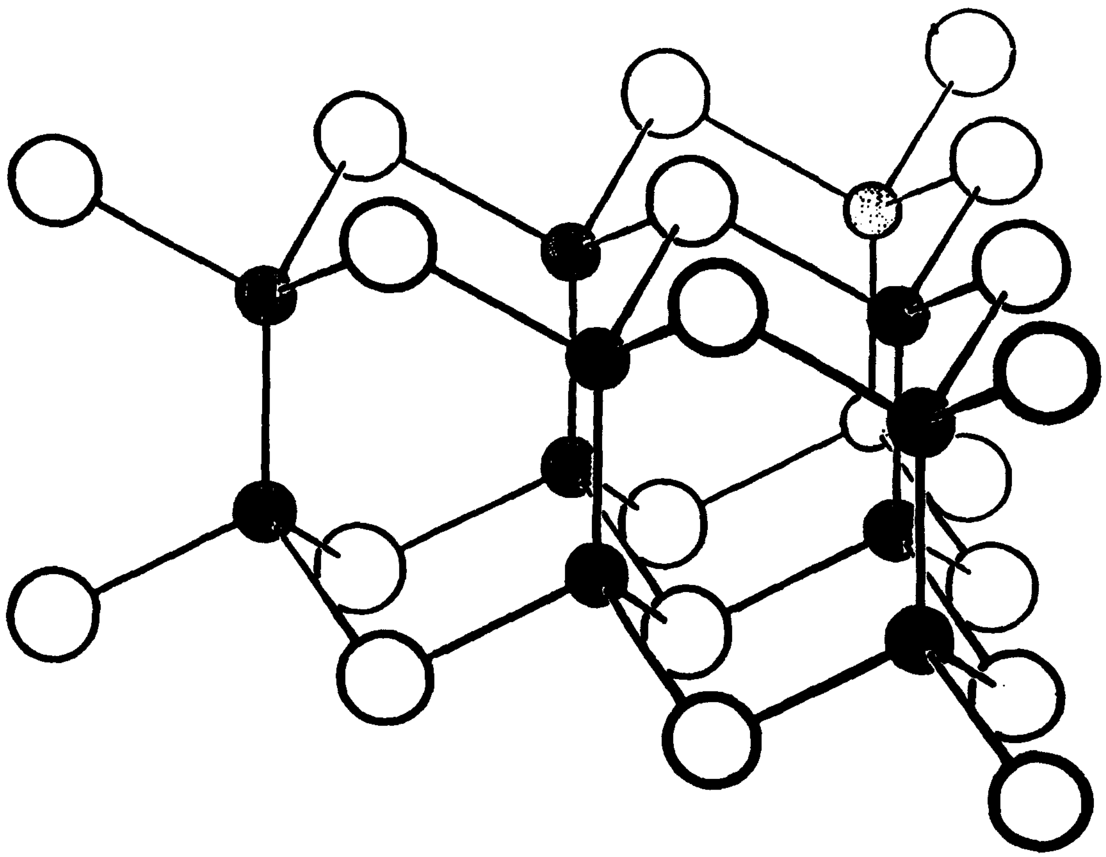
INTRODUCTION:

In the quest for solid state laser sources in the mid- and far- infrared wavelength ranges, a number of nonlinear crystals have been considered to frequency convert existing lasers into those ranges. One material which has been demonstrated to work in that range but has not been extensively studied for that purpose is gallium monoselenide (GaSe). It has a layered graphite type structure with a four-fold layer in the sequence SeGaGaSe. The crystals cleave very easily along the layers. See Figures 1 & 2.

GaSe has a number of very positive properties for nonlinear optical applications. Foremost among these is its extreme transparency. GaSe has a transparency range extending from a wavelength of 0.65 to 18 μm where the optical absorption coefficient does not exceed 1 cm^{-1} throughout the range. Its nonlinear optical coefficients are among the top five or so measured in the infrared (IR) for birefrigent crystals. Due to its large birefrigence, it can satisfy phase matching relations for parametric conversion from a wavelength of 1 to 18 μm. It also has the possibility for effectively converting sum and difference frequencies. Optically useful faces can be obtained by careful cleaving.

On the negative side, GaSe is a soft material with fairly low melting temperature. It readily cleaves on a 100 plane but is too soft to easily polish if other planes are needed. Under high optical power usage the material sags and deforms. With proper support and with side cooling, perhaps an effective device may be possible taking advantage of the desirable properties of the material.

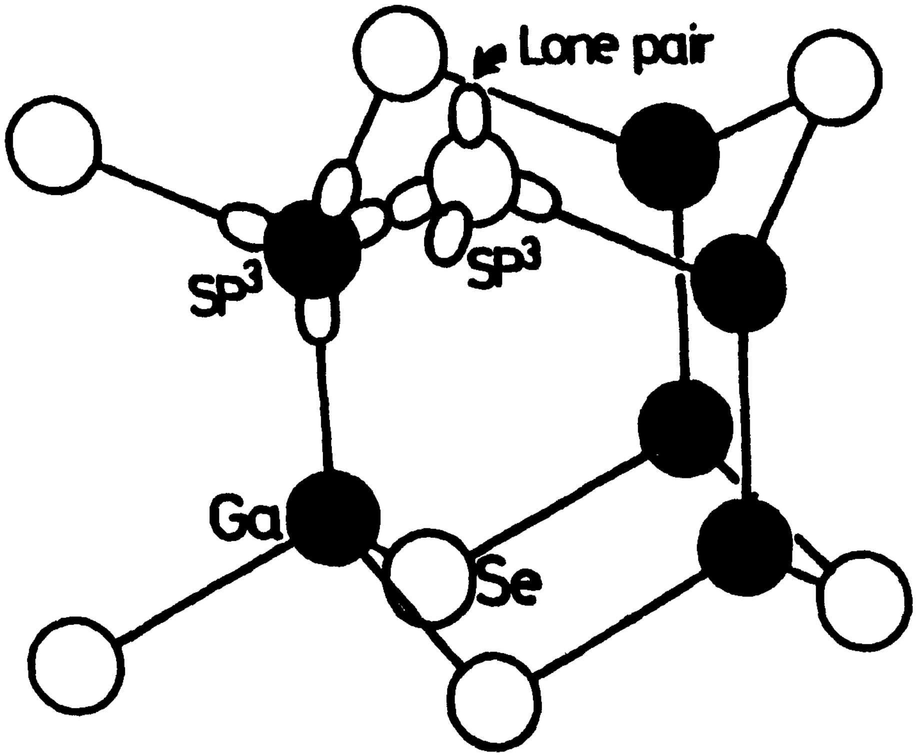
The purpose of this effort is to tabulate the published properties of GaSe, to list most of the papers published on this material (around 600), and to organize and condense this enormous amount of material. Needless to say, relevant material in some papers may have been overlooked. It should also be noted that no attempt was made to evaluate the quality of the published results.



Layer of GaSe. The Ga atoms are represented by the small shaded circles. the Se atoms by the large open circles.

E. Mooser & M. Schülter, Phil.Mag., 23 811 (1971)

Figure 1 Structure of GaSe



Atom configuration of a GaSe layered semiconductor. The open circles and the full circles represent Se atoms, respectively.

T. Tambo & C. Tatsuyama, Surface Science 222 343 (1989)

Figure 2 Structure of GaSe

2.0 STRUCTURE, GROWTH & MECHANICAL PROPERTIES OF GaSe

2.1 STRUCTURE AND GROWTH OF GaSe

This effort concentrates on gallium monoselenide, GaSe. The phase diagrams of Ga and Se were published by (Rustamov 1965), (Palatnik 1966), and (Dieleman 1971). Gallium and selenium can form the compounds gallium sesquiselenide, Ga_2Se_3, with a melting point >1020^{0}C; and gallium subselenide, Ga_2Se. Generally, I have tried to avoid papers dealing with these compounds but occasionally one may have gotten into the bibliography

The first record of synthesis of GaSe appears to be that of the work of (Klemm 1934). GaSe exists as hexagonal layers (See Fig.3) with several polytypes denoted as β, γ, δ and ε (Kuhn 1975), (Madelung 1992) and (Gouskov 1982). See Figures 4 & 5. (Hulliger 1976) and (Terhell 1975,1976) also discuss these polytypes. According to (Gouskov et al 1982), the β-type structure is the stable form of GaS and had not been reported for GaSe. (Wieting 1972) and (de Blasi Il Nuovo Cimento 1989) report work on β-GaSe. All of the following GaSe structures have a lattice spacing of a = 3.755 Å. The ε-type structure is a stable form of GaSe at room temperature with c = 15.95 Å. It is a hexagonal structure with space group P$\underline{6}$m^2. The γ -type structure is a rhombohedral structure of space group R3m with h = 23.92Å. The δ-type is a hexagonal structure of space group P6_3mc with c = 31.990 Å. It was discovered by (Kuhn 1975). Most of the papers covered in this work deal with the ε-type. This is a negative uniaxial crystal, $n_o > n_e$. Point group : $\underline{6}$2m or $\underline{6}\underline{m}$2 ($D_{3h}$). Table 1 is taken from (Madelung 1992).

Growth techniques for GaSe are covered in the article by (Gouskov 1982) and the book by (Givargizov 1987). Some other articles on crystal growth are by (Schubert 1955), (Bube 1959), (Beck 1961), (Basinski 1961), (Akhundov 1964), (Cardetta 1972), (Khalilov 1967), (Lieth 1977) and (de Blasi 1989). Vapor phase growth is covered by (Nitsche 1961), (Boelsterli 1962), (Terhell 1972,1975), (van Egmond 1974) and (Wiedemeier 1992). Crystals grown by the Bridgman method have ε-type structure with a variable amount of stacking faults. Crystals grown by vapor transport often form needle-like structures. GaSe thin film deposition is covered in (DiGiulio 1987), (Yudasaka 1988), (Aleksandrov 1989), (Kambe 1991), (Ueno 1991,1992), (Emery 1992), (Abe 1993), (Palmer 1993), (Brahim-Otsmane 1993) and (Fargues 1993). Growth of Fullerene thin films on a GaSe substrate is covered by (Sakurai 1993). There is some literature on the study of defects in GaSe crystals, viz. (Basinski 1961), (Guseinov 1967), (Mooser 1971), (Lendvay 1971), & (De Blasi Microscopy 1989,1991,1992).

2.2 **Molecular Weight:** (Minder 1976) 148.68

Table 1 : Properties of GaSe

3.10 III_x-VI_y compounds

3.10.1 III-VI compounds

GaS, GaSe and InSe crystallize in a hexagonal layer structure (Fig. 76, p. 116). The bonding is strongly covalent within the layers and weaker between them. Four basic polytypes are known (Fig. 77, p. 116). The GaTe lattice is a monoclinic distorted GaSe lattice (Fig. 78, p. 116).

Substance	Structure	Static and dynamical lattice parameters: a,c [Å]	d [g cm^{-3}], T_m [K], c_{ik} [10^{11}dyn cm^{-2}]	$\varepsilon(0)$, $\varepsilon(\infty)$	Band structure parameters: E_g [eV]	at T[K]	m [m_0]	Transport parameters: μ [cm^2/Vs]
GaSe	hexagonal layers	a : 3.755	d : 5.03	$\varepsilon(0)_\parallel$: 6.18	$E_{g,dir}$: 2.1275	4.2	$m_{n\parallel}$: 1.6	$\mu_{n\parallel,dr}$: 80
(several	β : D^4_{6h} - $P6_3/mmc$	c : 16···34	T_m : 1211	$\varepsilon(0)_\perp$: 10.6	2.021	300	$m_{n\perp}$: 0.5	$\mu_{n\perp,dr}$: 3000
polytypes)	γ : C^5_{3v} - R3m	depending	c_{11} : 10.24	$\varepsilon(\infty)_\parallel$: 5.76	$E_{g,ind}$: 2.103	4.2	$m_{p\parallel}$: 0.2	$\mu_{p\parallel,dr}$: 210
	δ : C^4_{6v} - $P6_3mc$	on polytypes	c_{12} : 3.24	$\varepsilon(\infty)_\perp$: 7.44			$m_{p\perp}$: 0.8	$\mu_{p\perp,dr}$: 60
	ε : D^1_{3h} - $P\bar{6}m2$		c_{33} : 3.07					$\mu_{n,H}$: 250
			c_{55} : 0.70					$\mu_{p,H}$: 50
			c_{66} : 3.5					

2.3 **Density:**

(Minder 1976) gives 5.03 g/cm^3

(Gatulle 1983) gives 5030 ±10 kg/m^3.

2.4 **Elastic Constants:**

(Khalilov 1967) were the first to measure elastic constants of GaSe using ultrasonic techniques. They show velocity versus temperature plots. In units of 10^{11} dynes/cm^2, their results are: $C_{11} = 10.24$, $C_{66} = 3.5$, $C_{33} = 3.07$, $C_{55} = 0.70$

and $C_{12} = C_{11} - 2C_{66} = 3.24$.

(Tanaka 1975) using Brillouin scattering, obtained in the same units as above:

$C_{11} = 10.5 \pm 0.4$, $C_{12} = -2.9 \pm 0.8$, $C_{13} = -3.32 \pm 0.12$,

$C_{33} = 3.57 \pm 0.08$, $C_{44} = -1.05 \pm 0.05$.

(Gatulle 1983) give their results and compare them with those of (Khalilov 1967), (Powell 1977), (Hamaguchi 1980), (Chiang 1978), and (Kovtun 1980). See Table 2.

Table 2. Elastic constants of GaSe

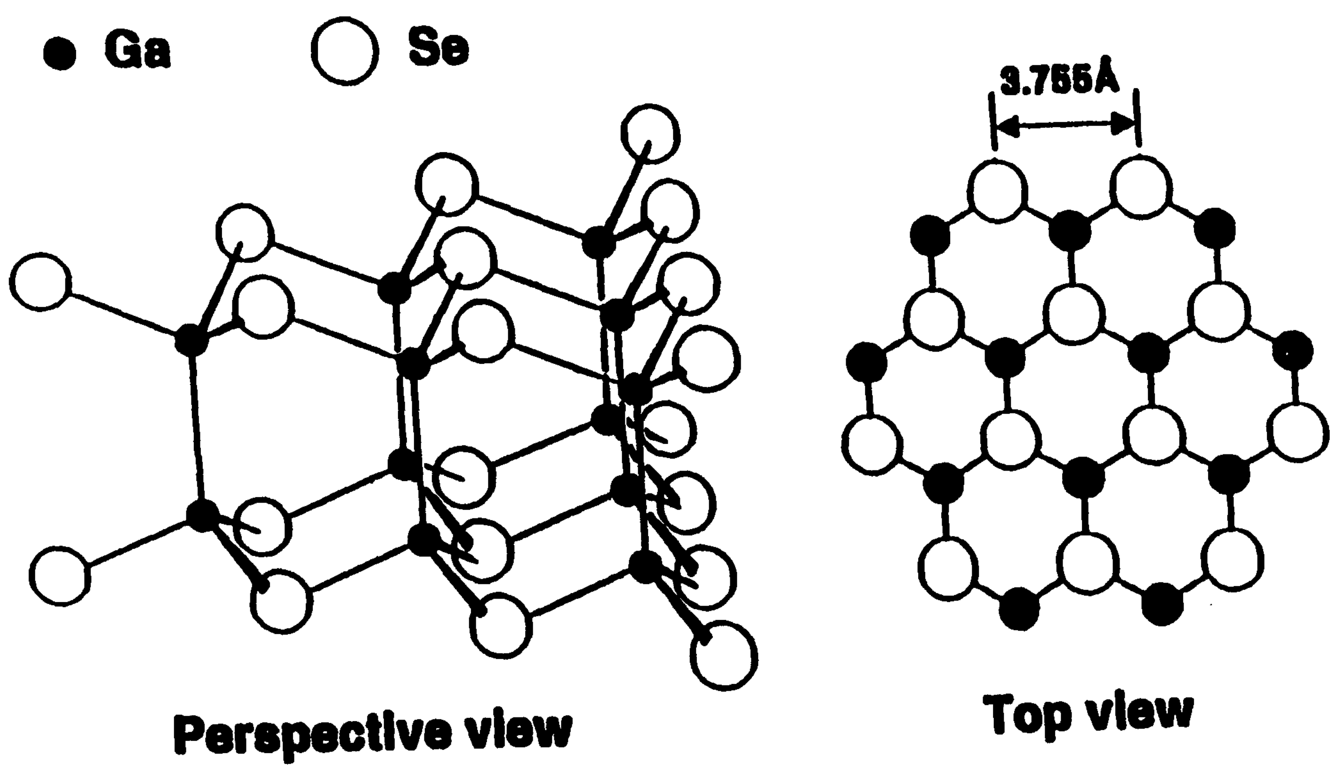
Elastic constants of GaSe (in 10^{10} N/m^2)

elastic constants	method					
	neutrons [1]	Brillouin [22]	[23]	ultrasound [24]	[25]	our results
C_{11}	9.4	10.5	10.5	10.2	10.17	10.33
C_{33}	3.18	3.57	3.51	3.07	3.872	3.41
C_{44}	1.25	1.05	1.04	0.70	0.92	–
C_{12}	–	2.75	3.25	3.24	2.73	2.89
C_{13}	–	1.22	1.26	–	1.17	–

[1] Powell 1977
[2] Hamaguchi 1979
[23] Chiang 1978
[24] Khalilov 1967
[25] Kovtun 1980

(Gatulle 1983) gives the pressure derivatives (dimensionless):

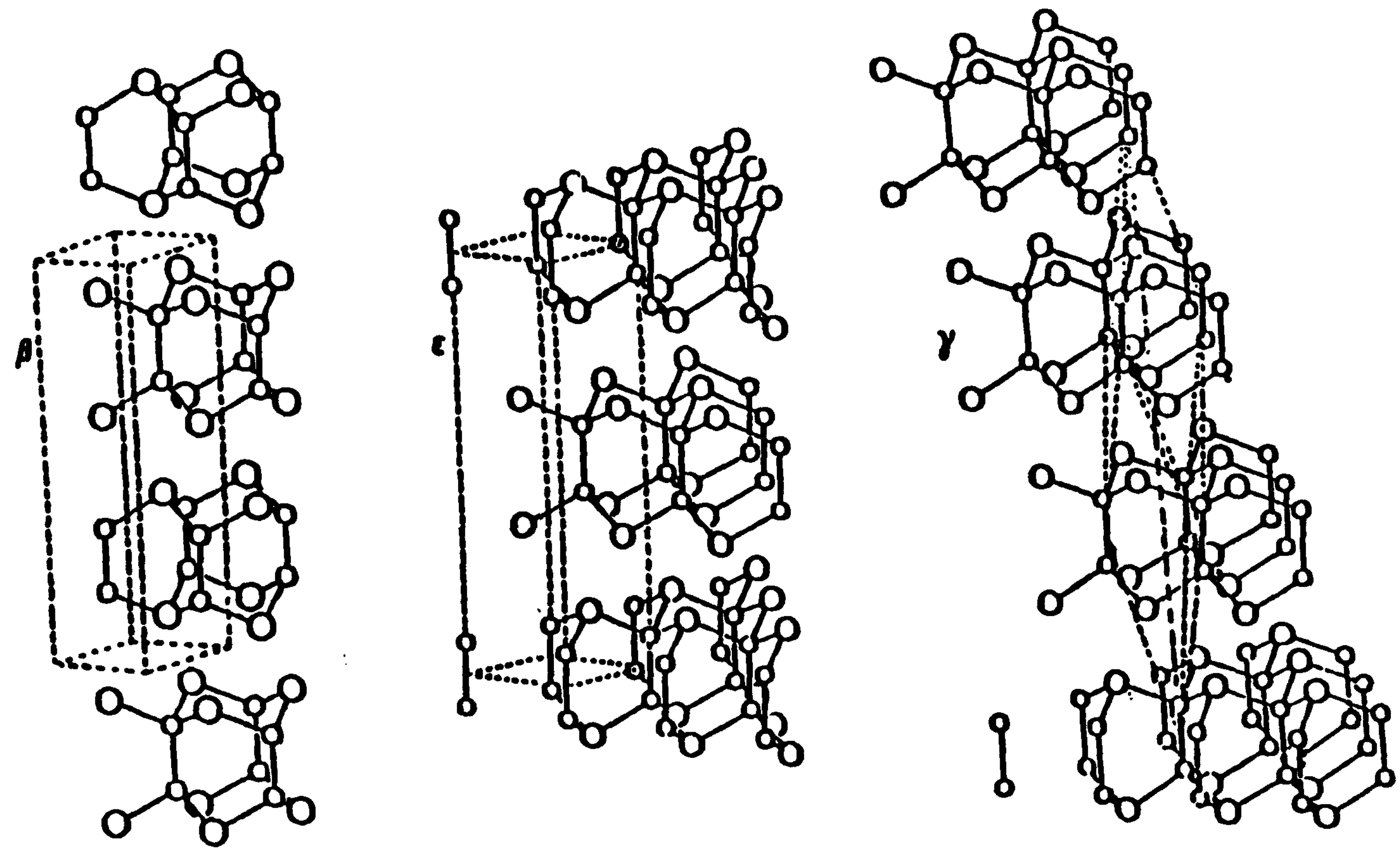
$$dC_{33}/dP = 19 \pm 1,\quad dC_{66}/dP = 1.9 \pm 0.4,\quad dC_{11}/dP = 8.4 \pm 0.6$$



Perspective and top views of a unit layer of GaSe.

Uneo,Abe, Suiki & Koma, Jap.J.Appl.Phys.Lett., <u>30</u> L1352 (1991)

Figure 3 Structure of GaSe



Crystallographic structures of the β, ε and γ polytypes of GaSe-like compounds. The unit cells are represented by the broken lines. They are hexagonal for the β and ε polytypes and rhombohedrical for the γ one.

Y. Depeursinge, Nuovo Cimento <u>64B</u> 11 81)

Figure 4 Polytypes of GaSe

POLYTYPES OF GaSe

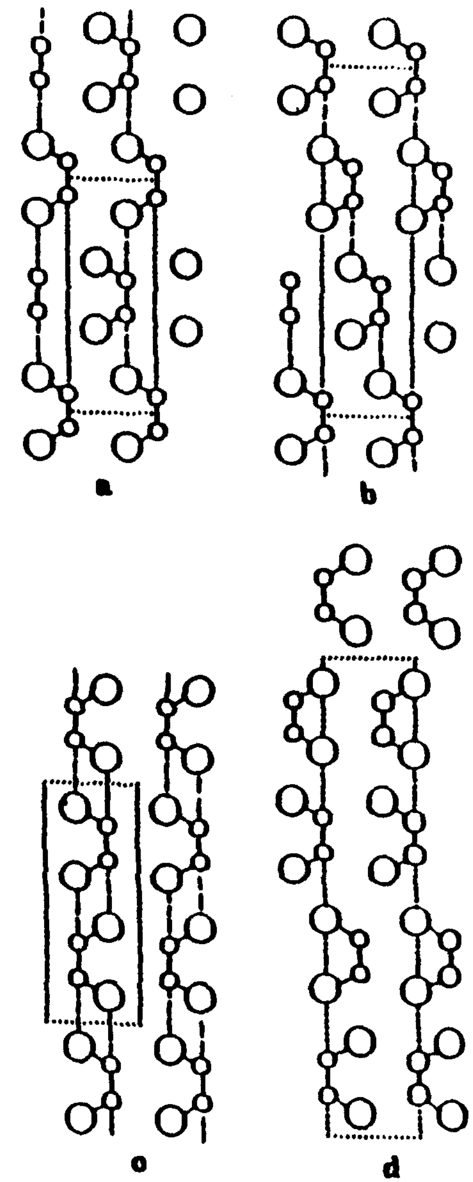


Fig.77. GaSe. Layer structure with cation pairs and tetrahedral cation coordination; (110) sections through the hexagonal cells. (a) ε-GaSe, (b) γ-GaSe, (c) β-GaSe, (d) δ-GaSe.

O. Madelung,ed. Semiconductors Other than Group IV and III-V Compounds (Springer 1992) p. 116

Figure 5 Polytypes of GaSe

2.5 **Brillouin Scattering:**

Papers concerned with Brillouin scattering are: (Chaing 1978), (Hamaguchi 1979), (Honma 1983), (Tanaka 1975), and (Yamada 1976, 1981).

2.6 **Raman Scattering:**

Papers concerned with Raman scattering are: (Abdullaev 1992), (Allakhverdiev 1980, 1986), (Altshul 1980), (Hamaguchi 1979), (Hayek 1973), (Hoff 1975), (Ibragimov 1989), (Irwin 1963), (Jandl 1978), (Kuroda 1987), (Le Toullec 1981), (Mercier 1974), (Raydellet 1979), (Seibert 1990), (Semjonow 1992), (Vinogradov 1980), (Wieting 1973), and (Yoshida 1973).

2.7 **Lattice Vibrations (Infra-red):**

(Finkman 1974)

3.0 THERMAL PROPERTIES OF GaSe:

3.1 Melting Point:

960 °C	(Rustamov 1965)
950 °C	(Palatnik 1965,1966)
938 ± 5 °C	(Dieleman 1971)
960 °C	(Cardetta 1972)
938± 3 °C	(Suzuki 1974)
960 °C	(Minder 1976)
936 °C	(Gouskov 1982)

3.2 **Specific Heat:** (Mamedov 1967) measured the specific heat of ε-GaSe from 60-300 K. In the range 60-87 K, the specific heat obeys $C_V = 0.329T^{1.00}$ J/mole deg. See Figure 6. It appears from the graph that, $C_P(300\ K) = 47.9$ J/(mole deg). (Jandl 1976) did further analysis of this data. See Figures 7 & 8.

(Mamedov 1978) gives in range 7-20 K, $C_V \propto T^3$;

for 20-30 K, $C_V \propto T^2$;

and as the temperature increases there is a gradual transition to $C_V \propto T$ with Debye temperature $\Theta_0 = 189 \pm 2$ K. See Figure 9.

Low-temperature (Aldzhanov 1989)

$\gamma = 0.01$ $\Theta = 431$ K

(Aliev 1972) gives $C_p - C_v = 0.690$ cal/mole deg at 300 K.

3.3 **Coefficient of Linear Expansion:** From (Aliev 1972) See Figure 10.

At 300 K, $\alpha_\perp = 10.8 \times 10^{-6}$/degree

$\alpha_{||} = 9.1 \times 10^{-6}$/degree

3.4 **Isothermal Compressibility:**

(Aliev 1972) See Figure 11.

At 300 K, $\chi_\perp = 0.66 \times 10^{-12}$ cm^2/dyne

$\chi_{||} = 0.27 \times 10^{-12}$ cm^2/dyne

(Polian 1982) gives $\chi_{||} = 24.9 \times 10^{-3}$ GPa^{-1}

$\chi_\perp = 5$

$\chi = 34.9$

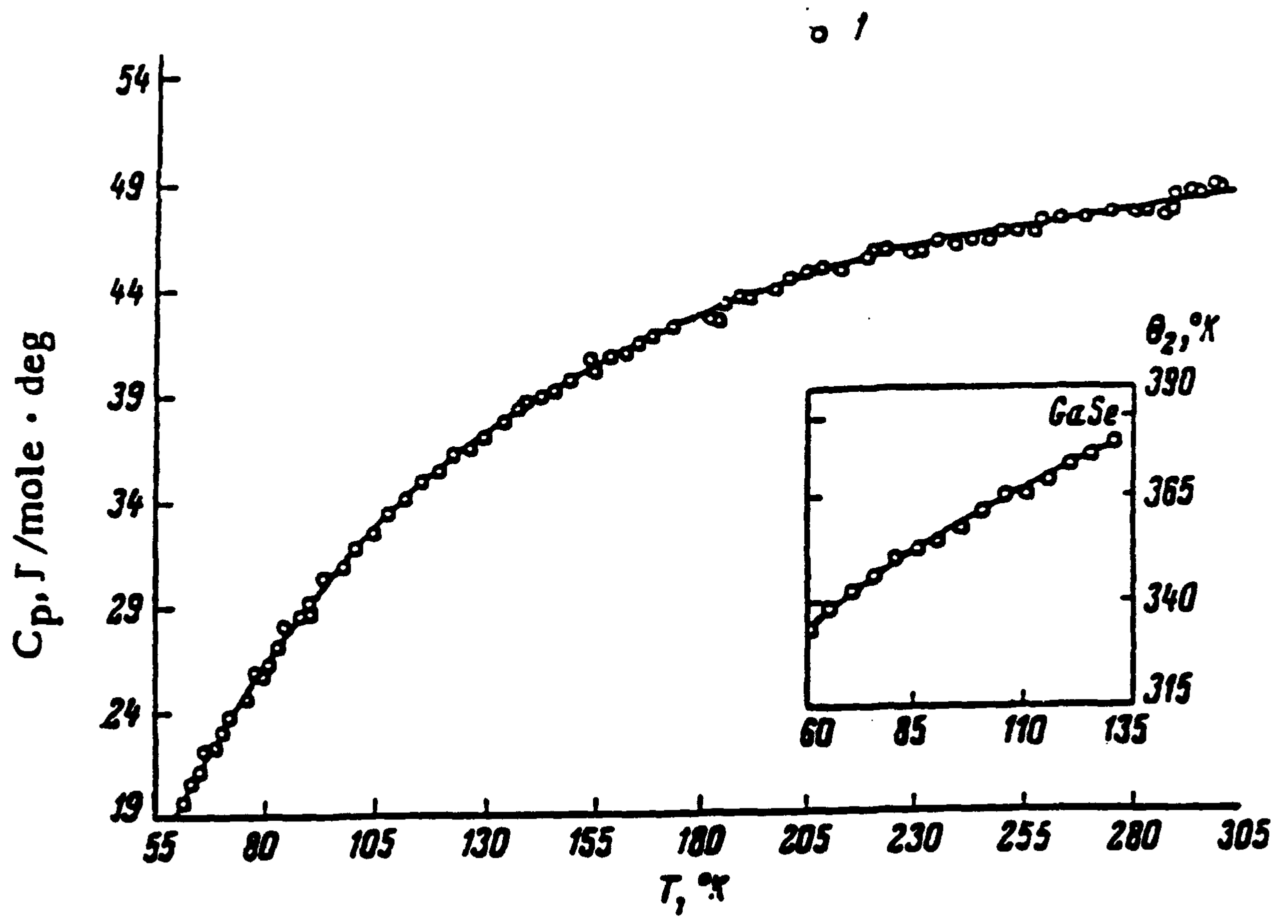
(Gatulle 1983) calculates compressibilities from his elastic constant data and obtains in units of 10^{-10} m^2/N:

B parallel linear compressibility = 0.256 ±0.018
B perpendicular linear compressibility = 0.052 ±0.005
B bulk compressibility = 0.0.360 ±0.028

3.5 **Grüneisen Parameter:** (Aliev 1972) See Table 3.

At 300 K, $\gamma_\perp = 1.07$

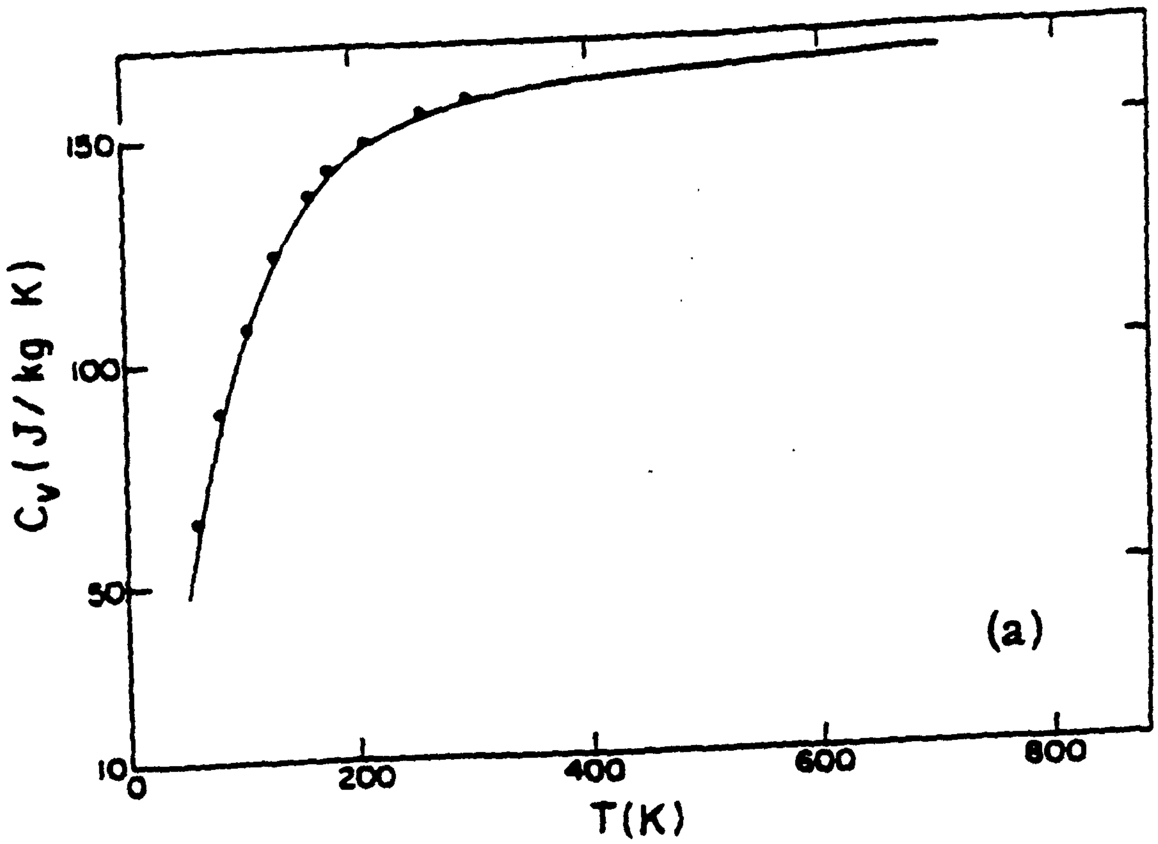
$\gamma_{||} = 2.35$



Temperature dependence of the specific heat of gallium selenide (1)

Mamedov et al, Sov.Phys.-Semiconductors $\underline{1}$ 363 (1967)

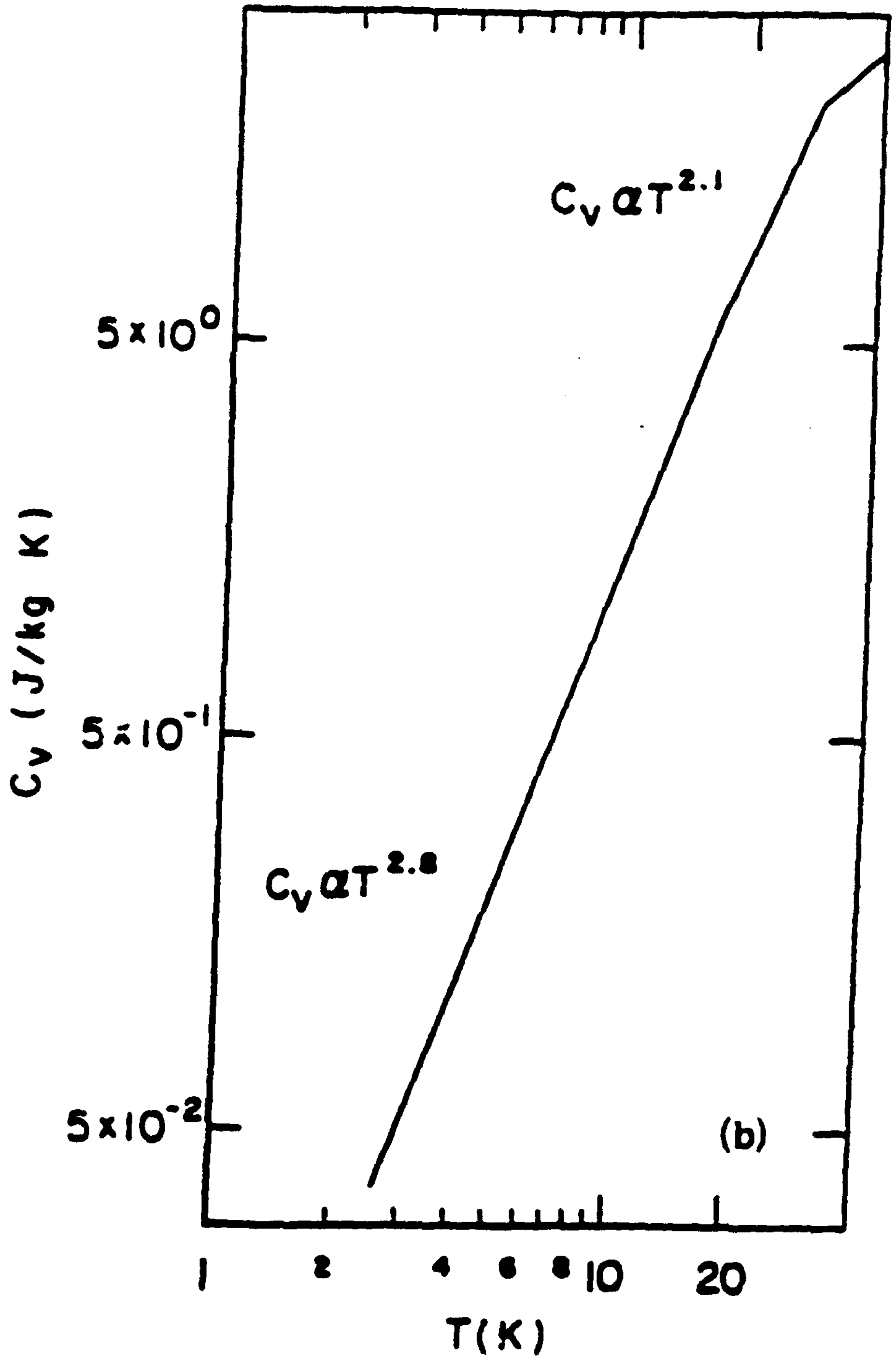
Figure 6 Temperature dependence of GaSe specific heat



(a) Temperature dependence of the specific heat $C_v(T)$ calculated from $g(\nu)$. The result of the calculation is shown as the solid line and the solid points represent the experimental measurements of Mamedov

Jandel et al, Phys. Rev. B13 686 (1976)

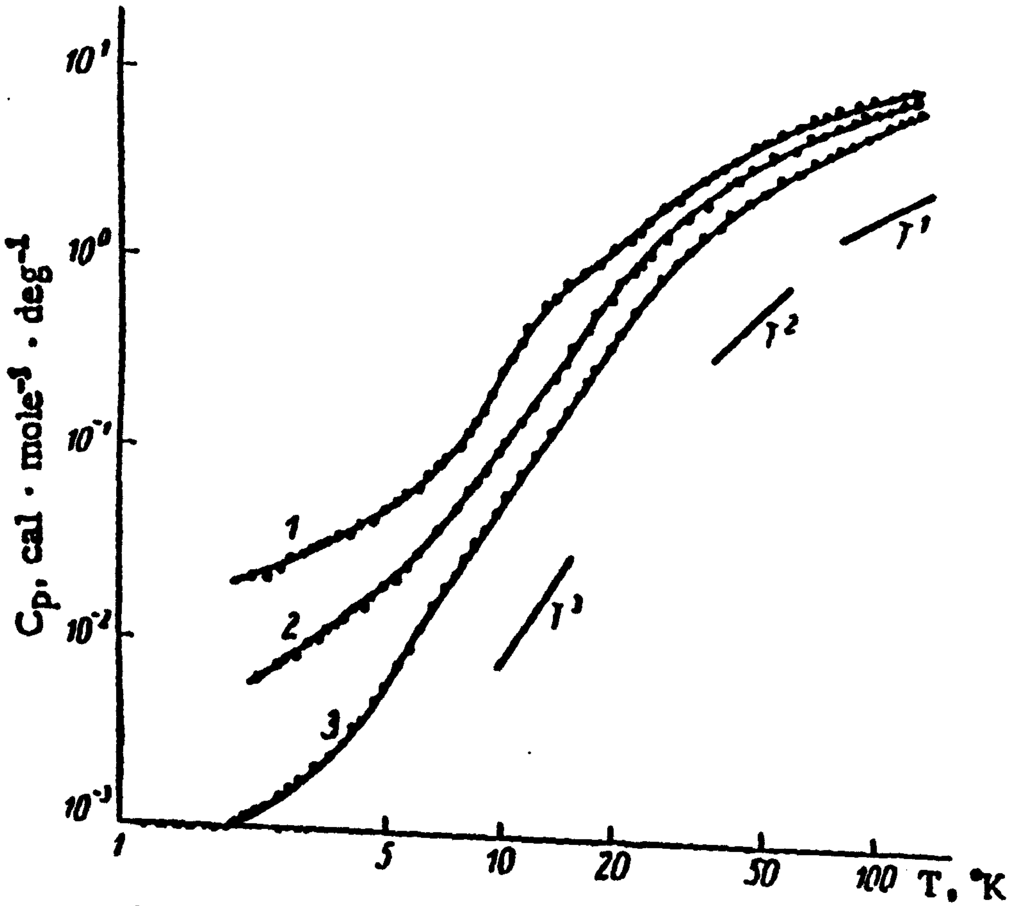
Figure 7 Temperature dependence of C_V of GaSe



Log-log plot of the temperature dependence of C_v at low temperatures.

Jandel et al, Phys. Rev. B13 686 (1976)

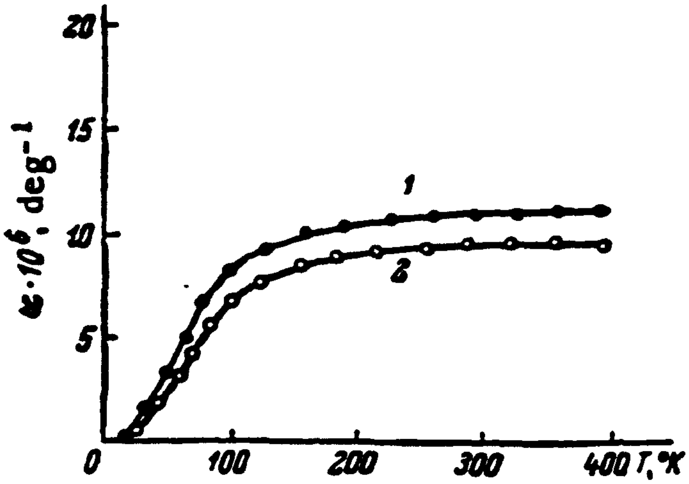
Figure 8 Cv of GaSe at low temperatures



Experimental results (shown on a logarithmic scale) for the specific heat of: 1) GaTe; 2) GaSe; 3) GaS.

Mamedov et al, Sov.Phys.- Solid State <u>20</u> 22 (1978)

Figure 9 Temperature dependence of specific heat of GaSe



The temperature dependence of the coefficients of linear thermal expansion $\alpha_{\perp}$ (1) and $\alpha_{\parallel}$ (2), measured perpendicular and parallel to the layers of a GaSe crystal.

Aliev et al, Sov. Phys.- Solid State 14 1304 (1972)

Figure 10 Temperature dependence of GaSe coefficients of linear expansion

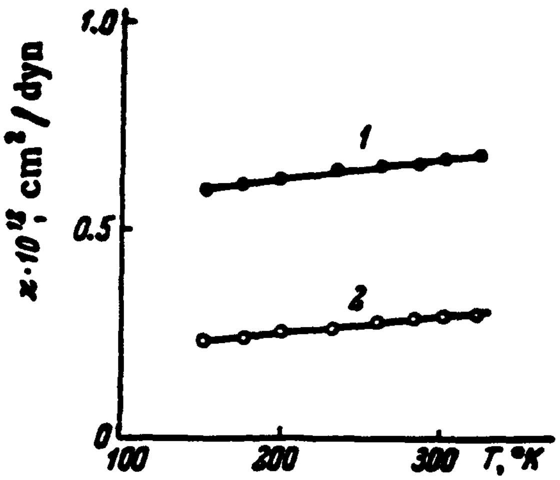


Fig. 2. The temperature of the coefficients of isothermal compressibility $\chi_{\perp}$ (1) and $\chi_{\parallel}$ (2), measured perpendicular and parallel to the layers of a GaSe single crystal.

Aliev et al, Sov. Phys.- Solid State 14 1304 (1972)

Figure 11 Temperature dependence of GaSe coefficients of isothermal compressibility

Table 3 C_P - C_V and Grüneisen Parameters for GaSe

The Value of the Parameters $C_p - C_v$, $\gamma_\perp$ and $\gamma_\parallel$

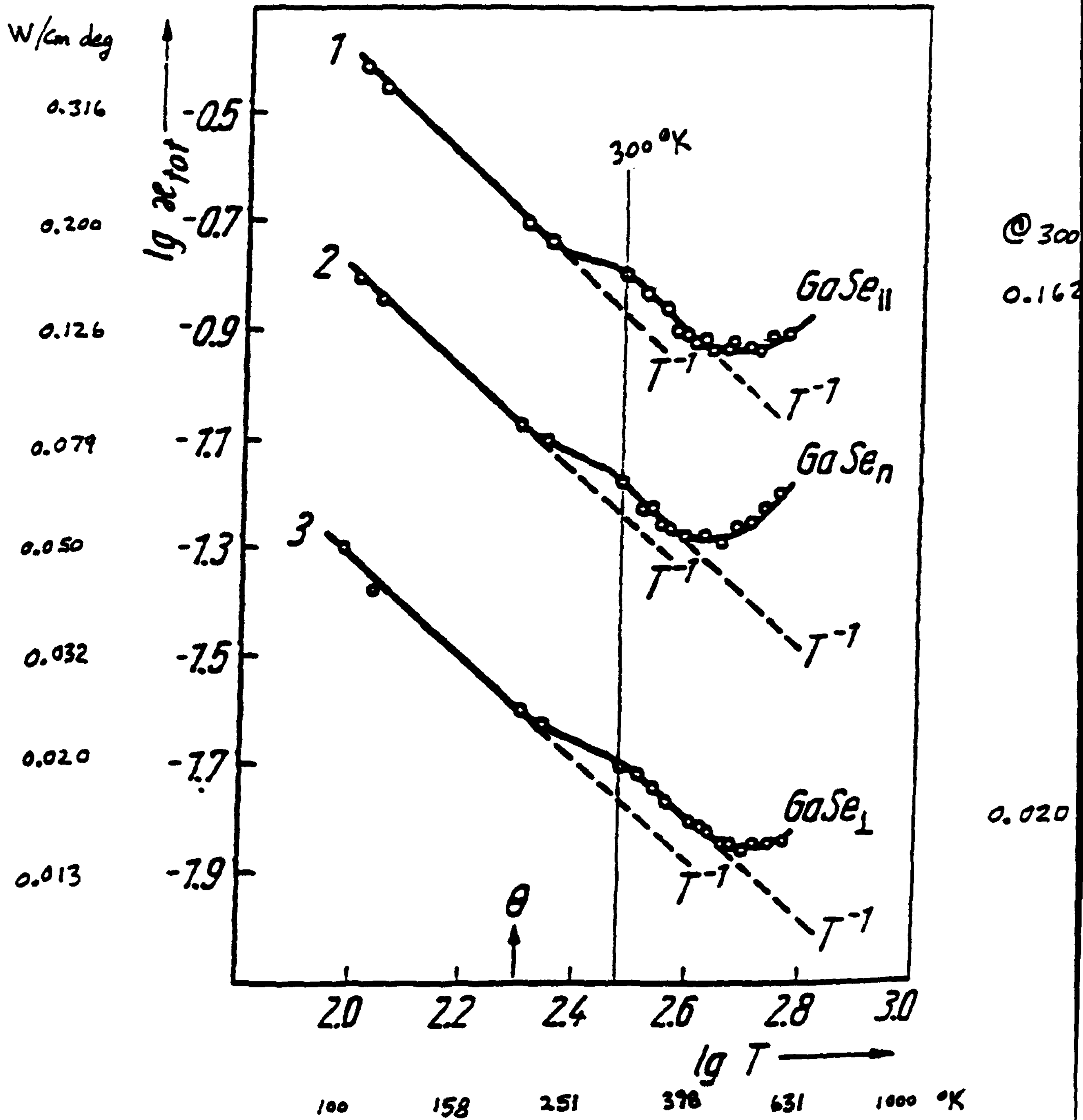
T, °K	$(C_p - C_v)$ calc. (cal/mole · deg)	$(C_p - C_v)$ [?] (cal/mole · deg)	$\gamma_\perp$	$\gamma_\parallel$
150	0.053	0.234	1.64	2.74
160	0.067	0.263	1.30	2.74
180	0.079	0.318	1.21	2.66
200	0.090	0.370	1.18	2.67
220	0.103	0.440	1.14	2.59
240	0.110	0.500	1.12	2.54
260	0.116	0.600	1.11	2.48
280	0.132	0.650	1.12	2.40
300	0.138	0.690	1.07	2.35

3.6 **Thermal Conductivity:** (Guseinov PL1966, PSS1966, 1967)
Plots from (PSS 1966) are in Figure 12.
From the curves, the heat conductivity at 300 K parallel to the [0001] axis is 0.162 W/cm deg, and perpendicular is 0.020 W/cm deg.

3.7 **Thermopower (Seebeck Coefficient):**

(Anis 1988) measured the diffusion thermopower parallel and perpendicular to the c axis in the temperature ranges 280-430 K and 250-330 K, respectively. At room temperature, $\alpha_{\parallel c}$ and $\alpha_{\perp c}$ were found to be the same, namely 120 ± 13 μV/deg. In the plot versus temperature, $\alpha_{\parallel c}$ exhibited a maximum at 435 K of 340 ± 20 μV/deg.

THERMAL CONDUCTIVITY of GaSe



Guseinov & Rasulov, Physica Status Solidi
<u>18</u> 911 (1966)

Figure 12 Temperature dependence of thermal conductivity of GaSe

4.0 ELECTRICAL PROPERTIES:

4.1 Band Structure:

Band structure papers are about evenly divided between theory and experiment. They are listed as follows: (Baltramiejunas 1991), (Balzarotti 1971), (Bassani 1964, 1967), (Belenkii 1979), (Bourdon 1974, 1976), (Depeursinge 1977, 1981), (Doni 1979), (Fischer 1963), (Hak-ping 1972), (Kamimura 1966, 1968), (Kowalczyk 1975), (Kuroda 1981), (Larsen 1976), (Margaritondo 1977),(McCanny 1977), (Ottaviani 1974), (Panfolov 1975), (Robertson 1979), (Schlueter 1972, 1976), (Sobolev 1982), (Thiry 1977), and (Williams 1977).

4.2 Resistivity (Electrical Conductivity) and Mobility:

(Fischer 1962) reports a perpendicular (to c axis) resistivity of 100 ohm-cm, a Hall coefficient of about 3000 cm^3/coulomb, and a mobility of 30 cm^2/V sec at 300K.

(Manfredotti 1974) gives a room temperature resistivity of 10^3-10^9 ohm-cm and mobilities of 215 cm^2/Vsec for holes and 60 cm^2/Vsec for electrons measured along the c axis.

(Minder 1976) gives mobilities parallel to the c axis at 300K as $\mu_e = 80$ cm^2/V sec and $\mu_h = 210$ cm^2/V sec.

The following papers deal with electrical conductivity and Hall mobility: (Abdullaev 1966, 1968), (Anis 1979, 1981, 1984, 1992), (Augelli 1977, 1978), (Capozzi 1977, 1981), (Fivaz 1967, 1976), (Gao 1988), (Ismailov 1966), (Kipperman 1971), (Manfredotti 1977), (Margaritondo 1977), (Mustafaeva 1988), (Nagat 1990), (Schmid 1974), (Tredgold 1969) and (Yudasaka 1988).

4.3 Effective Masses:

(Cingolani 1988) gives:

Direct gap (2.13 eV @ 10K)	$m_e = 0.23m_o$ $m_h = 0.4m_o$
Indirect gap (2.105eV @ 10K)	$m_e = 0.74m_o$ $m_h = 0.4m_o$

4.4 Photoconductivity:

Papers dealing with photoconductivity are listed as follows: (Abdullaev 1966, 1971), (Akhundov 1964), (Alekperov 1991), (Anis 1981), (Augelli 1981), (Belen'kii 1975), (Bube 1959, 1960), (Gross 1961), (Kawarada 1974), (Kyazymzade 1988), (Mekhtiev 1962, 1963, 1990), (Mozol' 1988, 1989), (Nazar 1981), (Niilisk 1969), (Ryvkin 1956), and (Tagiev 1987).

4.5 Dopants:

Effects of iodine doping are discussed in (Augelli 1979) and (De Blassi 1979).

Tin dopant increase the photosentitivity of GaSe. Papers on GaSe:Sn are: (Mekhtiev 1963), (Levialdi 1969), (Romeo 1969), (Abdullaev 1970), (Gadzhiev 1971), (Mustafaeva 1988), and (Salaev 1989).

(Shigetomi 1991,1993) discusses deep levels in Zn-doped p-GaSe.

Papers on various centers and traps are: (Manfredotti PRB & SSC 1974, 1975) and (Yamazaki 1993)

GaS_xSe_{1-x} solid solutions are discussed in (Belenkii 1975), (Camassel 1976), (De Blassi 1979), (Gavaleshko 1974), (Karamen 1970), (Kyazym-zade 1984), (Mercier 1974, 1976), (Schluter 1976), and (Yamaguchi 1984).

4.6 **Contacts:**

(Abdullaev 1966) discusses rectifying properties of p-GaSe single crystals.

Injection properties of minority carriers are covered by (Drapak 1989, 1990)

(Tambo 1989 a & b) discusses barrier formation and reactivity of contacts.

4.7 **Detectors:**

GaSe has been used in x-ray detectors (Castellano 1986) and in nuclear particle detectors (Manfredotti 1974,1975), (Mancini 1976), (Segura 1977), (Nakatani 1989), (Sakai 1988), and (Yamazaki 1988, 1993).

4.8 **Other Devices:**

(Mekhtiev 1978) describes a photo electric analyzer of polarized light using GaSe. A polarization sensitive photodiode at 632.8 nm based on photopleochroism (Mekhtiev 1990) is reported by (Manasson 1990).

(Hirlimann 1990) achieved a femtosecond optical gating.

A light modulator for 632.8 nm light is described by (Iwamura 1990, 1991).

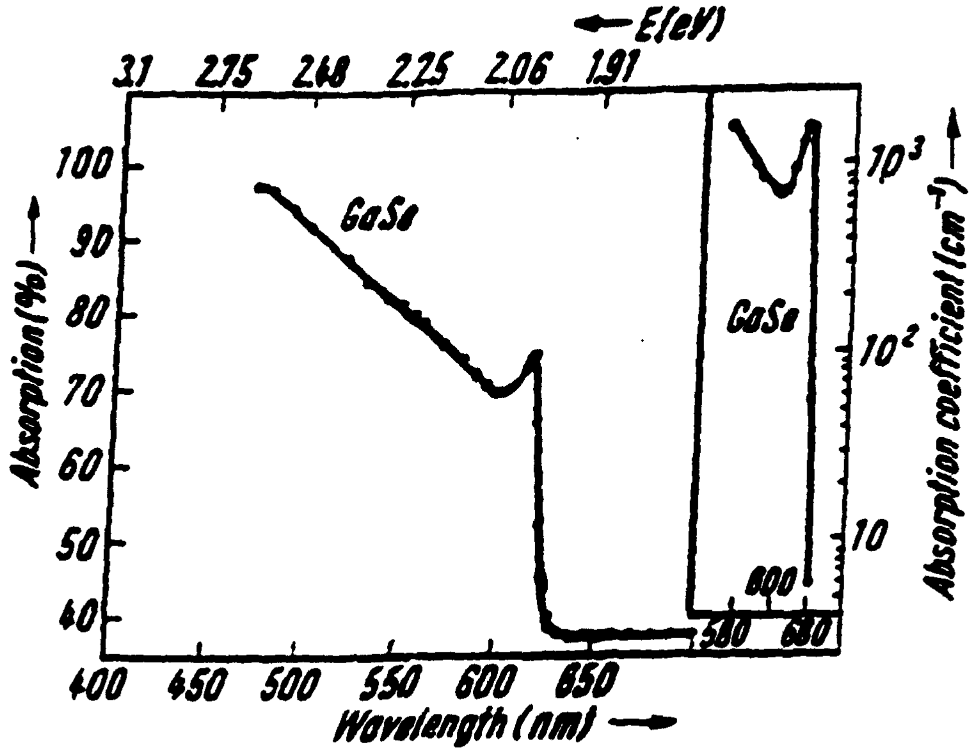
5.0 OPTICAL PROPERTIES:

5.1 Transmission, Optical Absorption Coefficient:

Crude measurements of the absorption edge of GaSe were obtained by (Gross 1959). (Fielding 1959) gave plots of the absorption coefficient from 450-900 nm at 78°K and 300°K apparently with unpolarized light. Plots of the absorption coefficient versus energy as a function of temperature are given in (Brebner 1962). A temperature dependence of the absorption edge was done by (Ismailov 1963). See Figures 13 & 14. The transmission spectra of GaSe at 300°K was given by (Akhundov 1966,1967). Figure 15. Transmission measurements from 0-20 µm at room temperature along with Sellmeier equations was given by (Abdullaev 1972). Figure16. This shows the transparency range as 0.65-18 µm. (Akhundov 1975) gives plots of the absorption coefficient versus wavelength (500-650nm) at various angles of incidence. (Le Toullec 1975) shows the absorption edges for δ- and ε-GaSe polytypes. The ordinary and extraordinary optical absorption coefficients for ε-GaSe between 443nm and 1.033µm were obtained by (Le Toullec 1977). Figure 17. (Antonioli 1977) shows plots of fitted extinction coefficients $k_{\parallel}$ and $k_{\perp}$ versus wavelength. (Antonioli 1979) shows plots of the absorption coefficient from 500 to 650 nm at 70, 175 and 290 K. Figure18. (Gusetnov PSS 1966) estimates the free carrier absorption (proportional to λ^2) at λ = 10 µm and T = 300 K to be 22.2 cm^{-1}. (Wasscher 1972) measured the optical absorption coefficient at various angles of incidence from 420-660 nm. (Abdullaev 1975) found many samples with absorption at 1.06 µm less than 0.25 cm^{-1}. A more recent transmission curve was published by (Bianchi 1978). Photoacoustic signals were shown in (Todorovic 1989). (Vodopyanov 1991) shows transmission curves with Fresnel losses denoted. Figure 19. Analyzing spectroscopic ellipsometry data, (Adachi 1992) shows plots of the extinction coefficient from 3-5 eV.

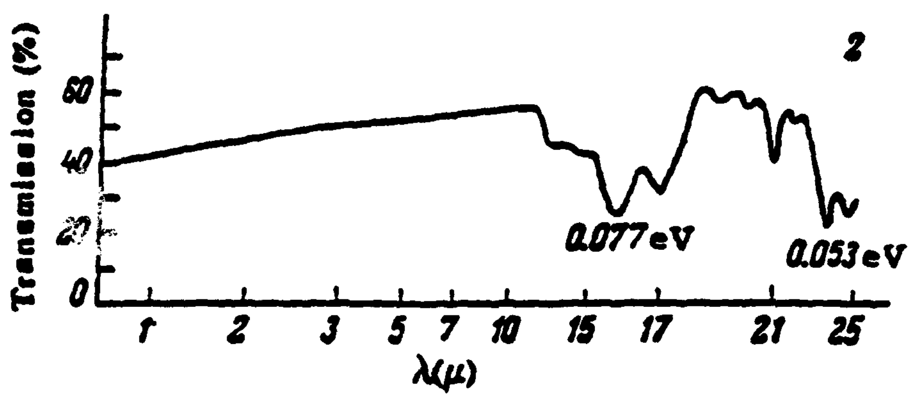
5.2 Reflection:

Reflection from single crystals was done by (Gasanova 1966). Figure 20. Later that year, they measured polarization effects in the ultraviolet reflection as well. Figure 21. (Akhundov 1966) also published results. (Leung 1966) shows reflectivity results in the infra-red. See Figure 22. (Nizametdinova 1967) published results of R^2 from 550-650 nm for E ∥ and ⊥ c, Figure 23. (Sobolev 1971) published some reflectivity measurements from 250-650 nm at 77 and 293°K. (Sobolev 1972) did uv reflectivity with apparently unpolarized light. Reflectance results in the range of 16-200 µm from 5-720°K was given by (Julien 1992). (Piacentini 1979) reports on reflectivity from 4-32 eV. (Sobolev 1990) gives reflection results using polarized light.



Akhundov et al, Physica Status Solidi 15 K109 (1966)

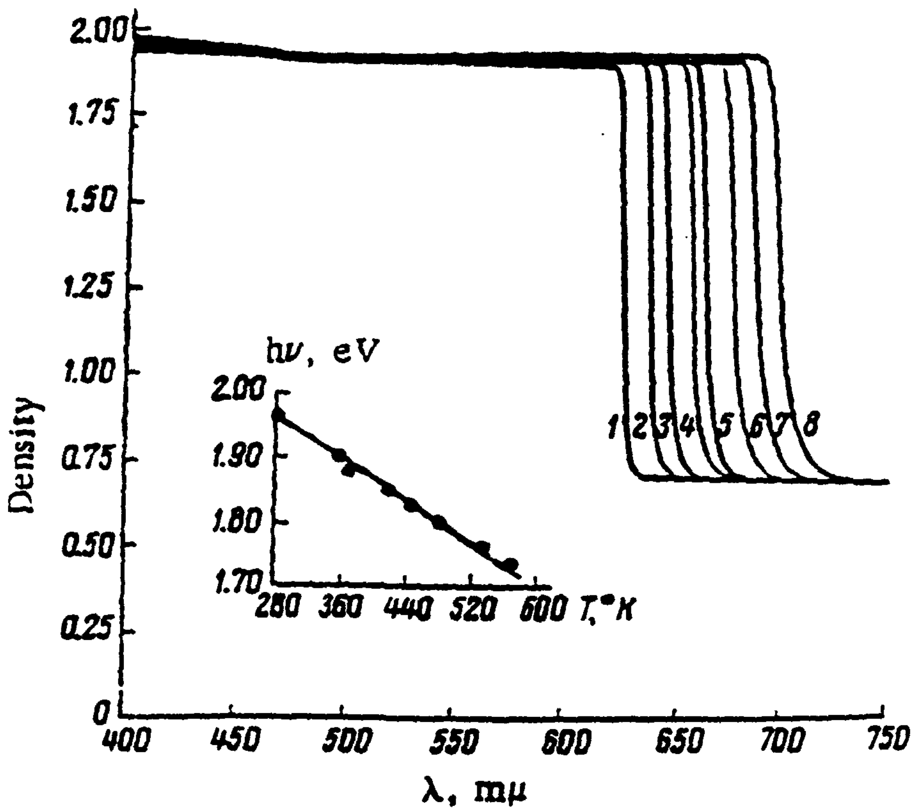
Figure 13 Absorption spectrum of GaSe at 300°K



Transmission spectra of single crystals of GaS (1) and GaSe (2) at 300°K.

Akhuundov & Kerimova, Optics and Spectroscopy 22 355 (1967)

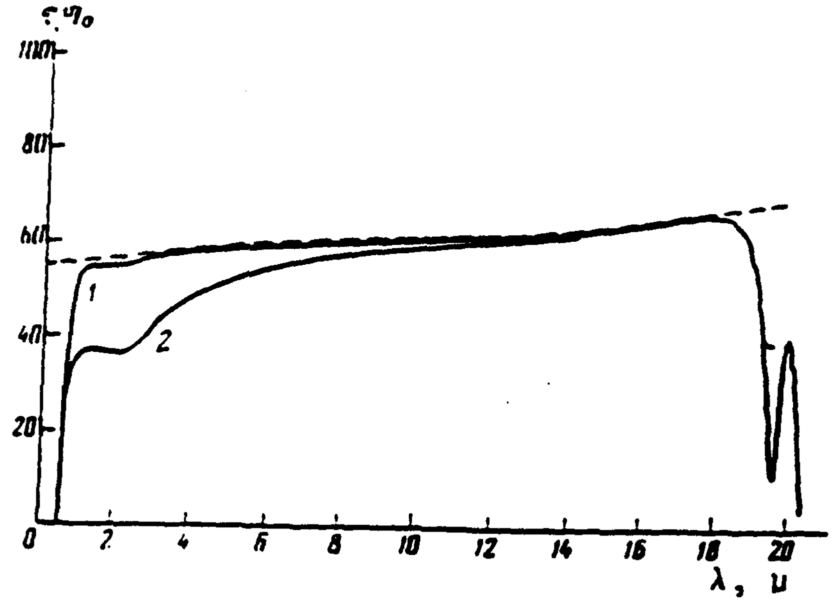
Figure 14 Transmission spectra of GaSe



Dependence of the optical density of gallium selenide on the wavelength at various temperatures T (in °K): 1) 283; 2) 335; 3) 370; 4) 414; 5) 445; 6) 494; 7) 536; 8) 578.

Ismailov et al, Soviet Physics- Solid State 5 2656 (1963)

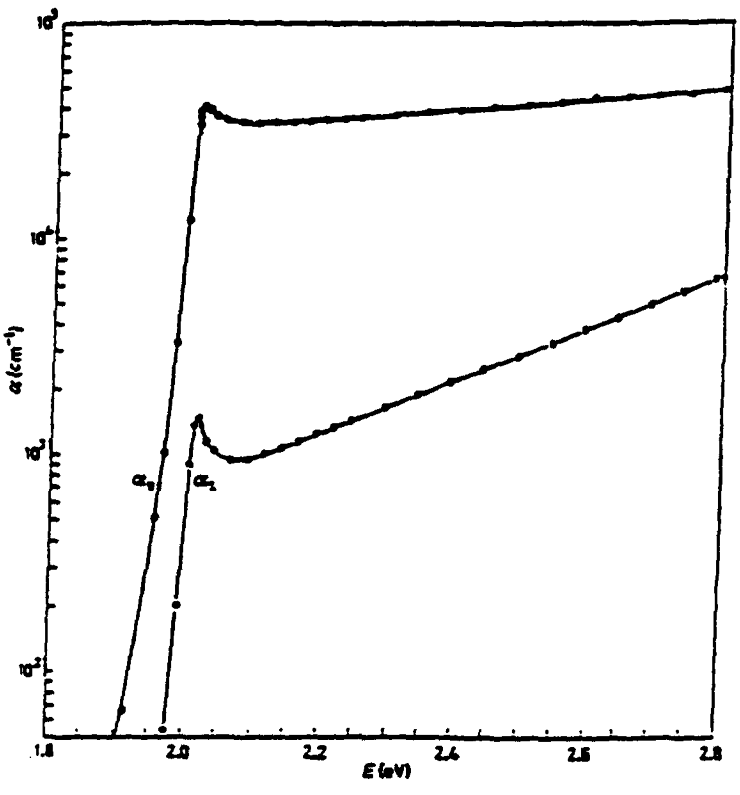
Figure 15 Temperature dependence of optical density of GaSe spectra



Transmission spectrum of GaSe crystal: dashed curves - reflection loss, continuous curves - transmission spectrum: 1 - sample thickness 1.5 mm, 2 - 6.0 mm.

Abdullaev et al Soviet Physics- JETP Letters **16** 90 (1972)

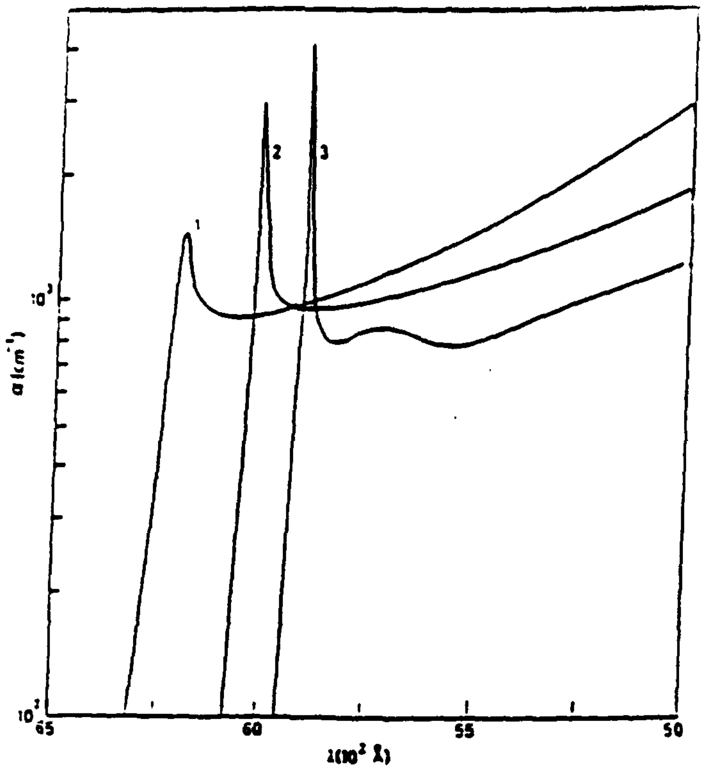
Figure 16 Transmission spectrum of GaSe



Ordinary and extraordinary absorption coefficient ($\alpha_{\perp}$ and $\alpha_{\parallel}$) of GaSe at room temperature *vs.* photon energy between 1.8 eV and 2.8 eV.

Le Toullec et al, Il Nuovo Cimento 38 B 159 (1977)

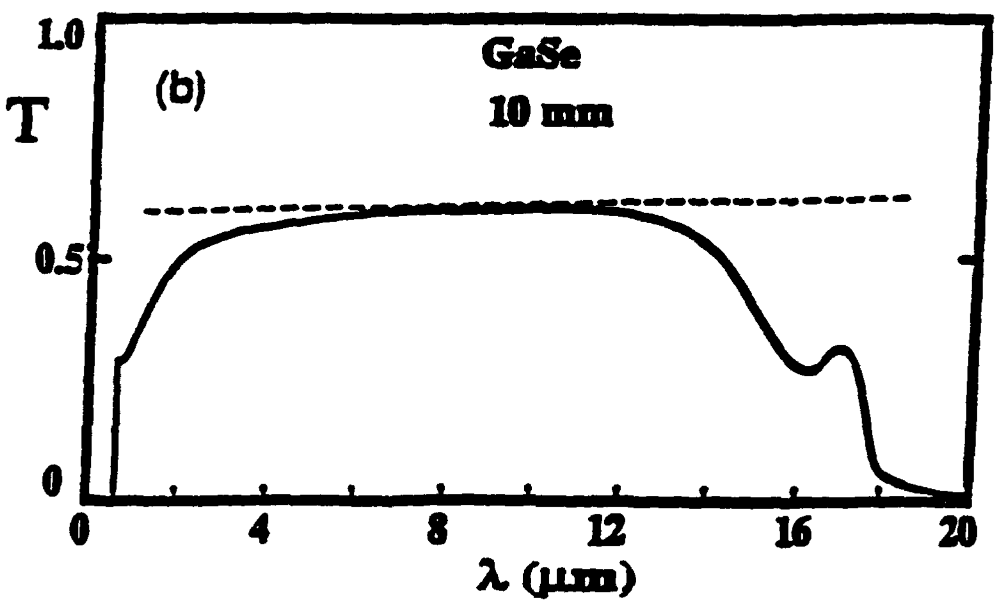
Figure 17 Ordinary and extraordinary absorption coefficient of GaSe



Absorption coefficient of GaSe for $T = 290$ K (curve 1), 175 K (curve 2), 70 K (curve 3).

Antonioli et al, Il Nuovo Cimento 54 B 211 (1979)

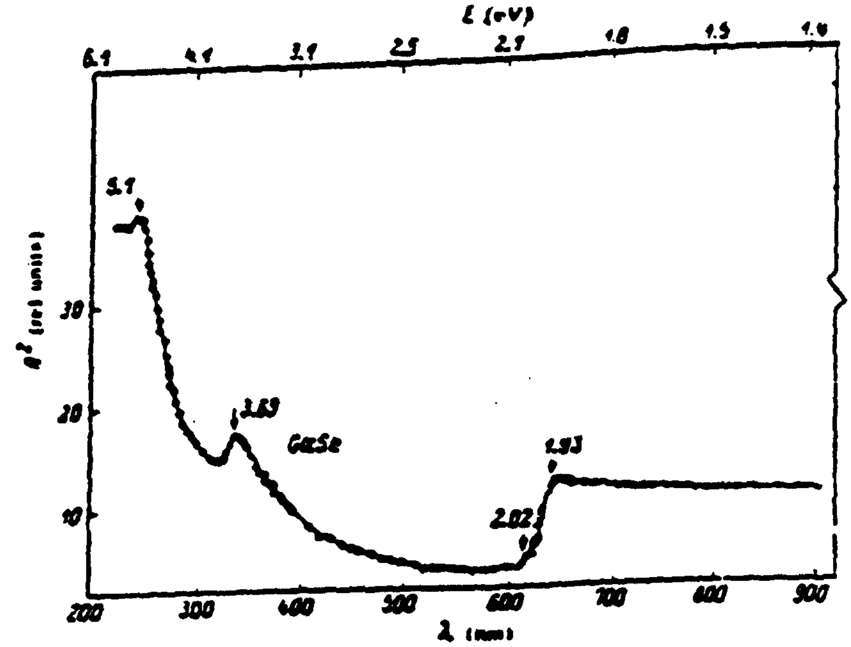
Figure 18 Absorption coefficient of GaSe at various temperatures



Transmission spectra taken at room temperature. (b) GaSe ($L = 10$ mm). Dashed curves, Fresnel losses.

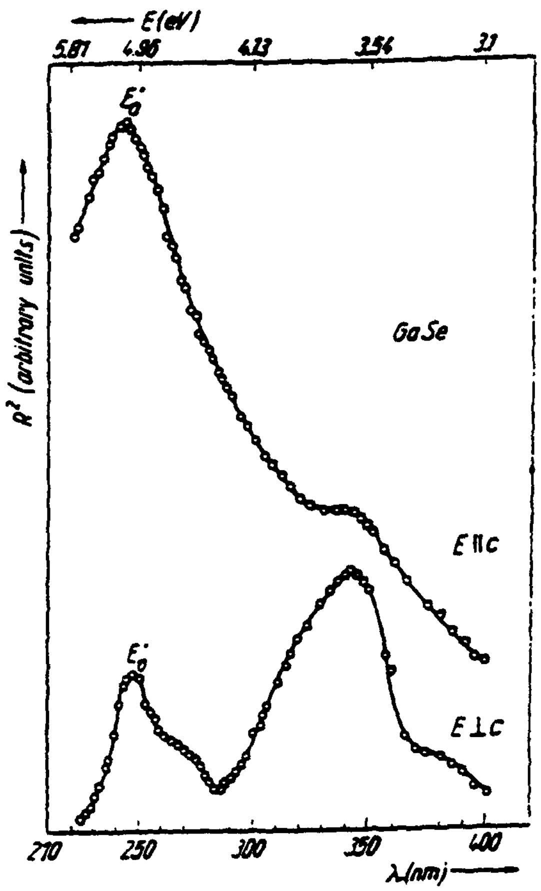
Vodopyanov, J.Opt.Soc.Am. B 10 1724 (1993)

Figure 19 Transmission spectra of GaSe



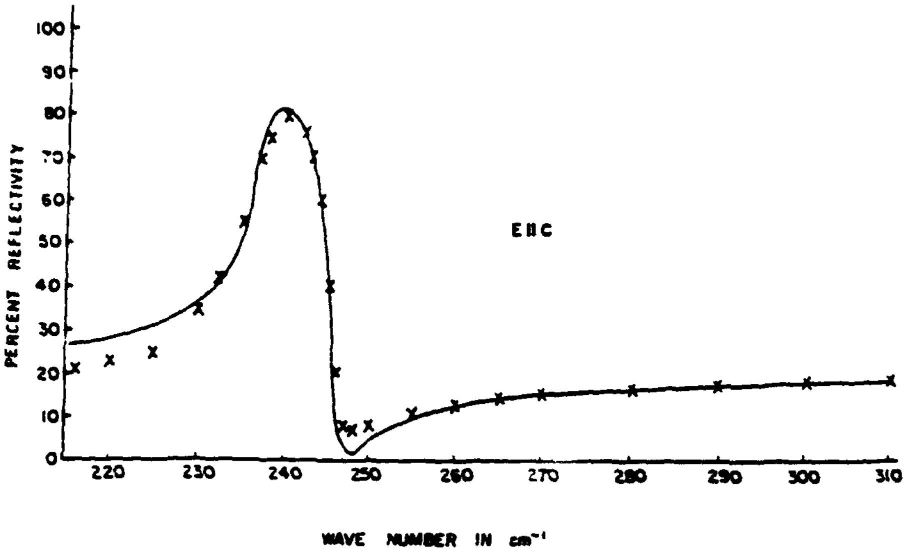
Gasanova & Akhundov, Optics & Spectroscopy 20 193 (1966)

Figure 20 Reflection spectra of single crystal GaSe at 300°K

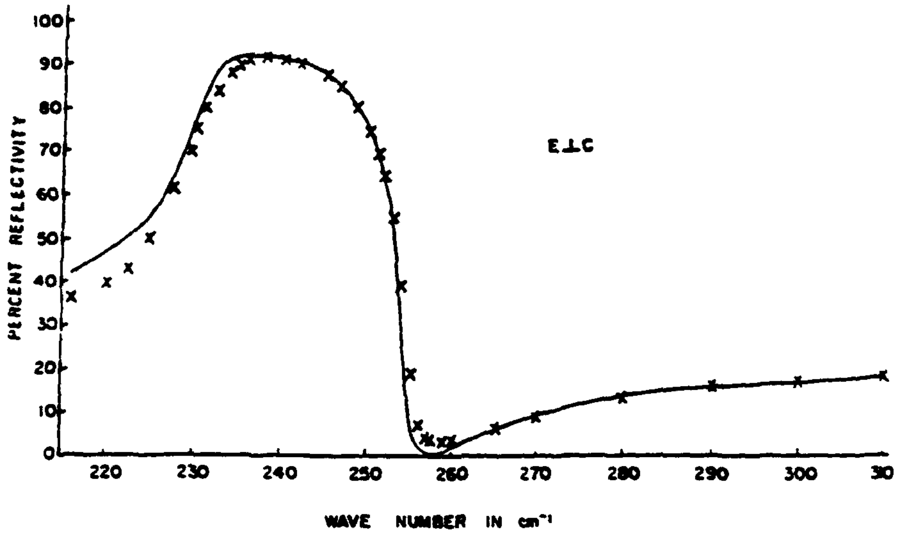


Gasanova et al, Physica Status Solidi 17 K115 (1966)

Figure 21 Reflection of GaSe at 300°K



Room temperature reflectivity of GaSe with $E \parallel c$. The crosses are the experimental points, and the curve is the reflectivity calculated with the dispersion parameters of Table 1.



Room temperature reflectivity of GaSe with $E \perp c$. The crosses are the experimental points, and the curve is the reflectivity calculated with the dispersion parameters of Table 1.

Leung et al, J. Phys. Chem. Solids 27 849 (1966)

Figure 22 Room temperature reflectivity of GaSe for $E_{\parallel c}$ & $E_{\perp c}$

5.3 **Band Gap:**

(Guriunova 1955) gives a gap of 1.95 eV.

(Nizametdinova 1967) finds $E_g = 2.0$ eV.

(Minder 1976) quotes (Bube 1960) at 300 K, reporting a gap of 2.03 eV.

(Ismailov 1963) gives the forbidden band width at room temperature as 1.97 eV. The temperature coefficient is $- 8 \times 10^{-4}$ eV/deg.

From reflection spectra (Nizametdinova 1967) finds $E_o = 2.0$ eV.

(Tatsuyama 1971) gives a bandgap of 2.138 ± 0.005 eV at 15°K.

(Abdullayeva 1977) describes how the gap is increased by alloying with S.

(Gauthier 1984) gives the pressure dependence of various gaps.

(Cingolani 1988) gives for the direct gap 2.13 eV at 10K occuring at the G point; for the indirect gap 2.105 eV due to the conduction band minimum at the M point.

5.4 **Index of Refraction:**

Index of refraction measurements on GaSe were first done by (Brebner 1965). See Figure 24. (Akhundov 1966) plotted results using unpolarized light. (Wasscher 1972) plots the various indices of refraction from 450-800 nm.

(Abdullaev 1972) gave the following Sellmeier equations:

$$n_o^2 = -0.05466/\lambda^4 + 0.48605/\lambda^2 + 7.8902 - 0.000824\lambda^2 - 0.00000273\lambda^4$$

$$n_e^2 = 6.0476 + 0.3423/(\lambda^2 - 0.16491) - 0.001042\lambda^2,$$ where λ is in µm.

(Abdullaev 1975) gives improved values for n_o:

$$n_o(\lambda = 0.63\text{mm}) = 2.993 \pm 0.005$$

$$n_o(\lambda = 1.15\text{mm}) = 2.899 \pm 0.005$$ and Sellmeier equations

$$n_o^2 = -0.06/\lambda^4 + 0.526/\lambda^2 + 8.038 - 0.00082\lambda^2 - 2.7 \times !O^{-6}\lambda^4$$

$$n_e^2 = 6.06 + 0.5754/(\lambda^2 - 0.453) - 1.04 \times 10^{-3}\lambda^2$$ where

λ is in microns. Several authors claim that the first set gave better fit to their data than the revised set, see e.g., (Bianchi 1978). (McMath 1976) gives the real parts of the ordinary and extraordinary for GaSe between 400 and 1000 nm. He also gives values for Sellmeier equation fits to the data. There was some follow up work in (McMath 1977). (Le Toullec 1977) gives the ordinary and extraordinary refractive indices for ε-GaSe between 774 nm and 1.033 µm. (Piccioli 1977) covers the refractive index between 450 nm and 330 µm at 300°K. (Lisitsa 1978) shows experimental plots of n_o and n_e from 750 to 500 nm at 300, 77 and 20.4 K.

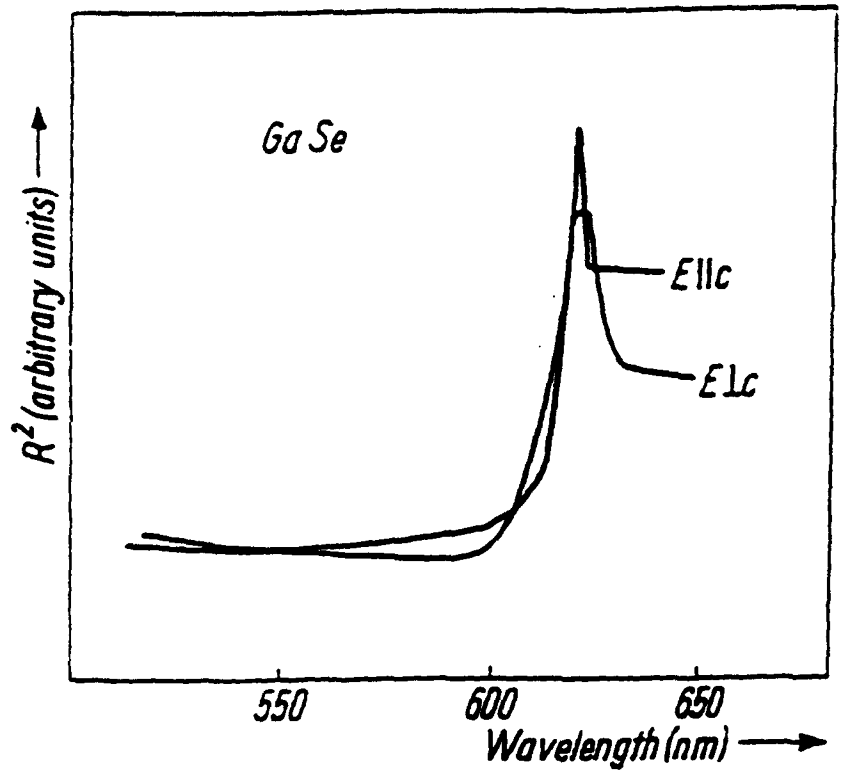
(Abdullaev 1989) still gives his revised Sellmeier equations to be the following:

$$n_o^2 = - 0.06/\lambda^4 + 0.526/\lambda^2 + 8.038 - 0.00082\lambda^2 - 0.0000027\lambda^4$$

$$n_e^2 = 6.06 + 0.5754/(\lambda^2 - 0.0453) - 0.00104\lambda^2$$ where λ is in µm.

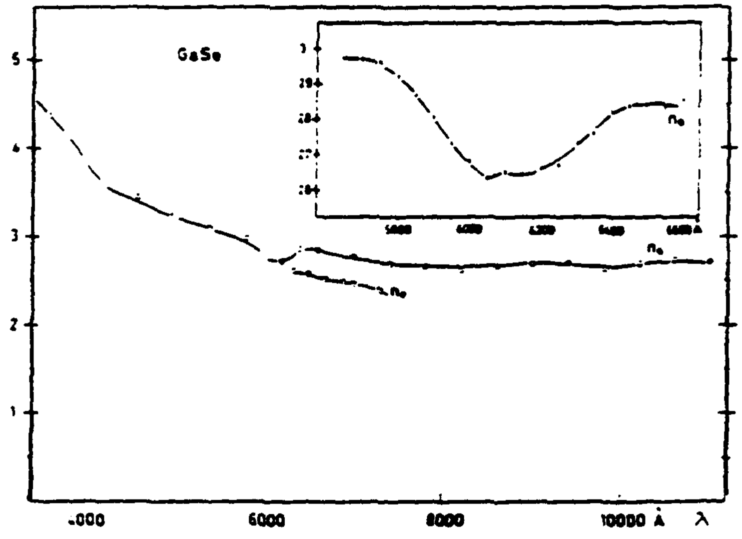
(Adachi 1992) plots indicies of refraction from 0.1-5 eV on ε-GaSe obtained from analysizing spectroscopic ellipsometry data.

(Barnes 1979) measured the temperature variation of the difference between the two indices of refraction at room temperature using a 10.6 µm CO_2 laser. For GaSe $(\partial n_2/\partial T - \partial n_1/\partial T) = 150 \times 10^{-6}$/°K.



Nizametdinova, Physica Status Solidi 19 K111 (1967)

Figure 23 Reflection spectrum of GaSe single crystal



Variation de n_0 et n_e en fonction de la longueur d'onde dans le GaSe. L'influence de la ligne excitonique est visible à 6100 Å dans la courbe de détail.

Brebner & Deverin, Helvetica Physica Acta 38 650 (1965)

Figure 24 GaSe n_o and n_e versus wavelength

(Vodopyanov 1993) gives $n_o(\lambda=3\mu m) = 2.85$, $n_e = 2.46$. He also uses Abdullaev's first Sellmeier equations.

5.5 **Laser Damage:**

(Abdullaev 1975) found for CO_2 100 ns pulses a damage threshold of 30 MW/cm^2.

(Nikogosyan 1977) quotes (Abdullaev 1975, 1976) as follows: Surface damage threshold:

λ μm	τ_p nsec	I W/cm^2
0.694	25	2×10^7
1.06	10	3.5×10^7

(Sreckovic 1985) did work with a Nd:YAG laser. In the Q-switched mode with 17 ns pulses, no damage was observed with fluences of 1.72×10^5 J/m^2. For 100 μsec CW, the mode polarized normally at 300 mJ produced bigger craters than the free generation mode at 370 mJ. (Sreckovic 1989) continued the work showing pictures of various types of craters.

(Abdullaev 1989) found for CO_2 wavelengths there was no difference in threshold for a maximum power density of $I_\omega = 25$ MW/cm^2 with a pulse repetition frequency of 2 or 20 Hz. The peak breakdown intensity in MW/cm^2 for a 0.0024 cm^2 area was 33; for a 0.0059 cm^2 area, 28.

(Soileau 1990) used a CO_2 laser of SHG crystals [for type 1 (ooe) the phase matching angle is 14.5°]. For 150 ns pulses, the damage threshold was about 10 J/cm^2 with conversion efficiency $E(2)/E(1) = 0.33\%$. The maximum fluence reached with 100 ps pulses was about 2 J/cm^2 and showed no damage. Conversion efficiency was 3%.

(Vodopyanov 1991,1993) reports laser damage thresholds for $\lambda = 3$ μm, 100 ps pulses. Volume damage was observable. The damage threshold was 30 GW/cm^2 (energy fluence, 3 J/cm^2).

5.6 **Luminescence:**

In GaSe, most luminescence effects occur in the 580-620 nm region. Around 60 papers have been published. They are :
(Abdullaev 1971,1973,1982), (Agekyan 1976, 1978), (Akhundov 1965,1966,1970), (Anno 1979), (Bagaev 1979), (Bagirov 1975), (Balitskii 19882), (Baltramiejunas 1977), (Belen'kii 1975, 1976), (Bobrysheva 1990), (Brebner 1966), (Capozzi 1981,1983,1991,1993), (Catalano 1975,1977), (Chung 1988), (Cingolani 1973, 1987), (Coletti 1991), (Dobynde 1988), (Gnatenko 1987,1988), (Gross 1961), (Guseinov 1980), (Karaman 1970, 1972), (Kawarada 1974), (Kuroda 1975,1976), (Lee 1986), (Lu 1988), (Matsumura 1977), (Meneses 1976), (Mercier 1973,1976), (Minami 1990, 1992), (Mozol' 1985, 1988, 1989,1990), (Romeo 1971), (Sasaki 1975), (Sasaki 1973), (Schmid 1974), (Schwabe 1978), (Shaklee 1973), (Shigetomi 1991, 1993), (Springford 1963), (Staehli 1985), (Tagiev 1984), (Tatsuyama 1977), (Taylor 1987), (Ugumori 1972, 1976, 1977), (Voitchovsky 1972, 1973, 1974), (Yao 1983), and (Yu 1990).

5.7 **Excitons:**

Exciton effects occur near the absorption edge of GaSe. Since this region is in the 580-630 nm range, it is out of the infrared range. About 100 papers have been published on excitons in GaSe and are listed as follows: (Abdullaev 1973,1977), (Abddullaeva 1975), (Akhundov 1970), (Alekperov 1990), (Alekperov 1990), (Anno 1979), (Antoci 1973), (Aoyagi 1966), (Balitskii 1982), (Balzarotti 1971, 1972), (Belen'kii 1975, 1976, 1977), (Bernier 1987), (Besson 1977), (Bianchi 1973, 1975), (Bosacchi 1976), (Brebner 1967), (Brodin 1966,1986), (Capozzi 1981,1983,1985,1991,1993), (Catalano 1975, 1976), (Cavenett 1979), (Dawson 1979), (Dneprovskii 1986, 1988), (Dzhafarova 1991), (Forney 1977), (Gavaleshko 1974), (Gerlach 1975), (Gnatenko 1983, 1987, 1990), (Grant 1972), (Grandolfo 1971), (Gross 1961), (Halpern 1966), (Hasegawa 1965), (Hirlimann 1989, 1990), (Hvam 1989), (Kamimura 1969), (Karamen 1970, 1972), (Kovalyuk 1992), (Kuroda 1976), (Kyazym-zade 1992). (Leite 1972), (LeToullec 1980), (Lisitsa 1978), (Lukanyuk 1989), (Mercier 1975, 1976), (Minami 1990, 1992), (Mooser 1973), (Morigaki 1978), (Nikitine 1963), (Nakao 1968,1969), (Panfilov 1975), (Pavesi 1987, 1988, 1989), (Piccioli 1989), (Razbirin 1978), (Salaev 1972,1981), (Sasaki 1981), (Schwabe 1978), (Serizawa 1980), (Sobolev 1982, 1990), (Sokolov 1972, 1974), (Solomonov 1980, 1985), (Staehli 1980), (Subashiev 1970, 1971), (Subbotin 1972), (Taylor 1987), (Thanh 1978), (Ugumori 1976, 1977), (Vandyshev 1989), (Voitchovsky 1974), and (Zhang 1988).

5.8 **Electro-Optic Coefficient:**

(Sokolov 1972) measured the linear electro-optic coefficient at room temperature in the photon energy range 1.25-1.96 eV (990-632 nm). See Figure 25. At l = 0.63 µm, the value of $|2n_o^3 r_{22}| \approx 44 \times 10^{-10}$ cm/V.

5.9 **Nonlinear Properties:**

The use of GaSe as a nonlinear optical material was first suggested in the paper by (Abdullaev 1972). They present plots of the phase synchronism angles versus pump wavelength for second harmonic conversion. See Figure 26. Various wavelength versus angle plots of parametric radiation are given . See Figure 27. For the crystal symmetry, they obtain:

$$d_{eff} = - d_{22} \cos\Theta \sin 3\Phi \qquad (e = o + o)$$

$$d_{eff} = - d_{22} \cos^2\Theta \sin 3\Phi \qquad (e = e + o)$$

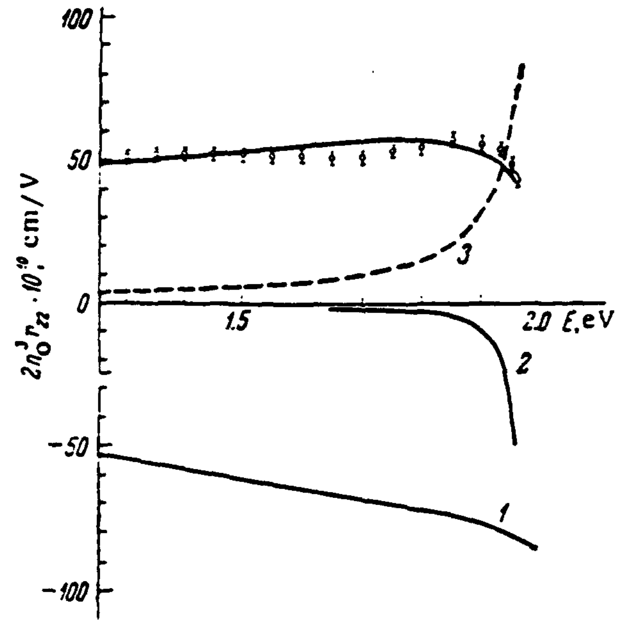
where Θ is the angle between the wave vector **k** of the pump radiation and the optic axis of the crystal(z). Φ is the angle between the crystal XZ plane and the kZ plane. Using e = o + o with CO_2, CO and $CaF_2{:}Dy^{2+}$ lasers, they obtained

$$\Theta(\lambda=2.36\mu m) = 18^o 40' \pm 10'$$

$$\Theta(\lambda=5.3\mu m) = 10^o 10' \pm 20'$$

$$\Theta(\lambda=10.6\mu m) = 12^o 40' \pm 20'.$$

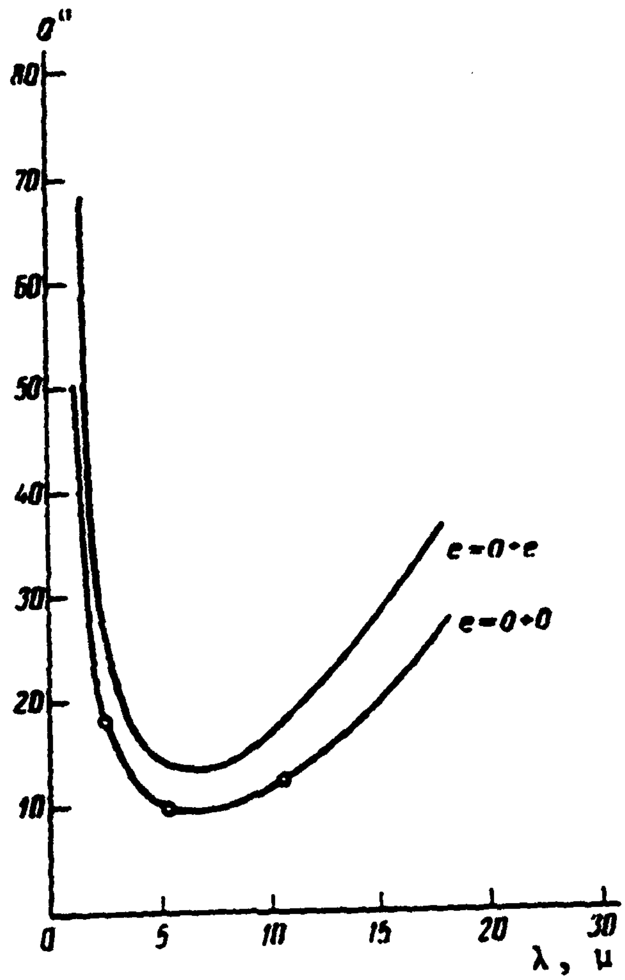
Also for SHG of 10.6µm, they measured $d_{22}(GaSe)/d_{31}(CdSe) = 3 \pm 0.6$, taking $d_{31}(CdSe) = 0.68 \times 10^{-7}$ cgs esu, yields $d_{22}(GaSe) = 2.0 \times 10^{-7} \pm 0.4$ cgs esu.



Dependence of $|2n_o^3 r_{22}|$ on the photon energy. The continuous line represents the theoretical dependence plotted for the values of A, B, and D given in text. The depencences of the components of $|2n_o^3 r_{22}|$ on the photon energy are represented by the numbered curves: 1) electron contribution; 2) exciton contribution; 3) exciton-electron contribution.

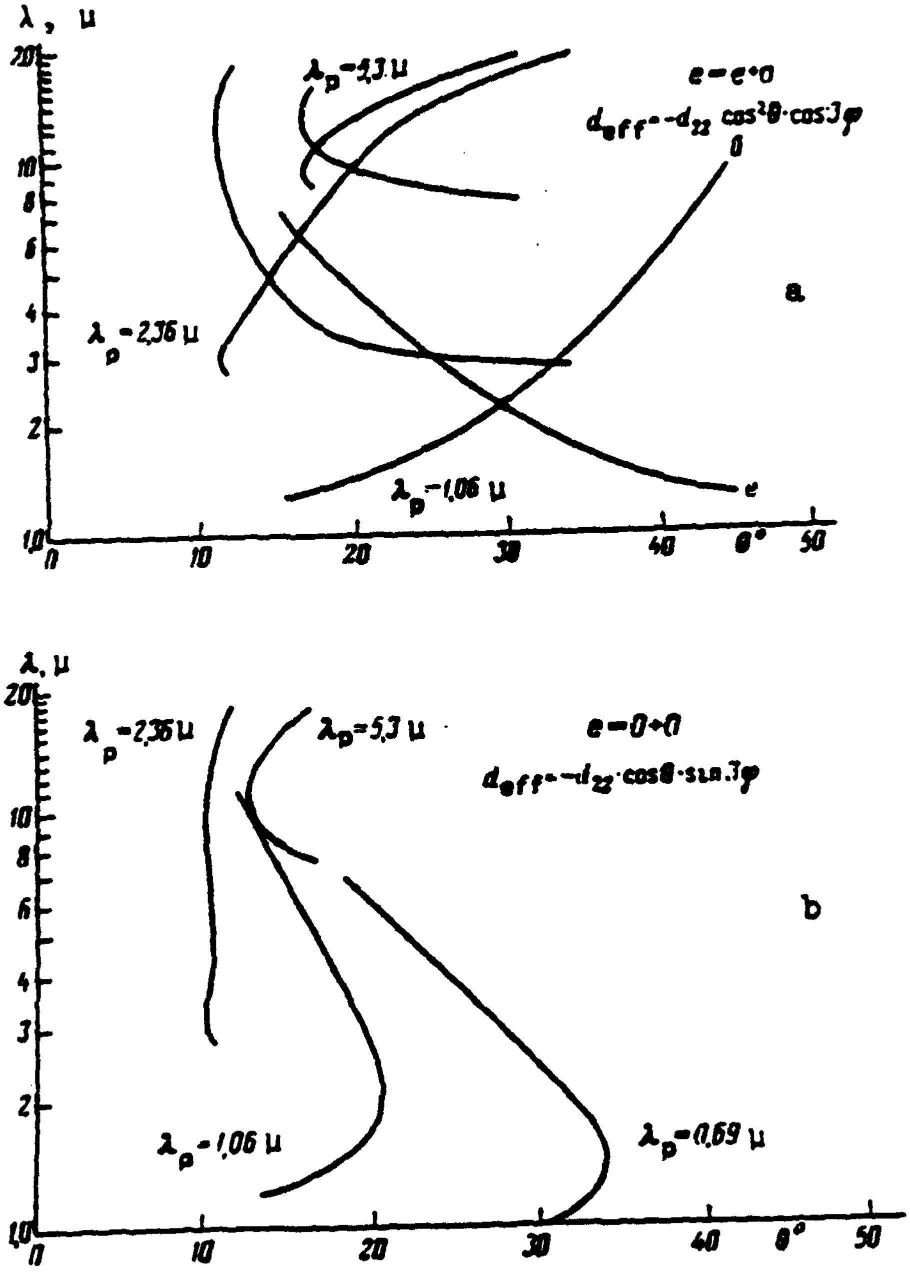
Sokolov & Subashiev, Sov. Phys.- Solid State 14 178 (1972)

Figure 25 GaSe electro-optic coefficient versus photon energy



Abdullaev et al, Sov. Phys.- JETP Letters 16 90 (1972)

Figure 26 Dependence of the GaSe phase synchronism angle for the second harmonic on the pump wavelength.



Abdullaev et al. Sov. Phys.- JETP Letters 16 90 (1972)

Figure 27 Wavelength versus angle curves of parametric radiation for different pump wavelengths on GaSe.

(Akhundov 1973) made measurements at several laser wavelengths using d_{36}(KDP)=1 as their reference. They state that for GaSe, $-d_{22} = d_{21} = 0.5\ d_{16}$. @$\lambda$=0.69$\mu$m, d_{16} (GaSe)= 2160 and d_{14}(GaAs)=570. The absolute value d_{36}(KDP) = 6 x 10^{-9}cgs esu. @λ=1.06μm, d_{16}(GaSe) = 1360 and d_{14}(GaAs)= 330 in KDP units. @λ=10.6μm, d_{16}(GaSe) = 272 and d_{14}(GaAs) = 210 in KDP units.

(Kupecek 1974) used GaSe for sum and difference frequency conversion of CO and CO_2. They obtained d_{22}(GaSe)/d-(proustite) = 4.9 $\pm$ 0.7 which yields d_{22}(GaSe) = 180 x 10^{-9} esu when taking d-(proustite) = 37 x 10^{-9} esu and d_{31}(CdSe) = 53 x 10^{-9} esu. Also, they summed YAG and CO_2.

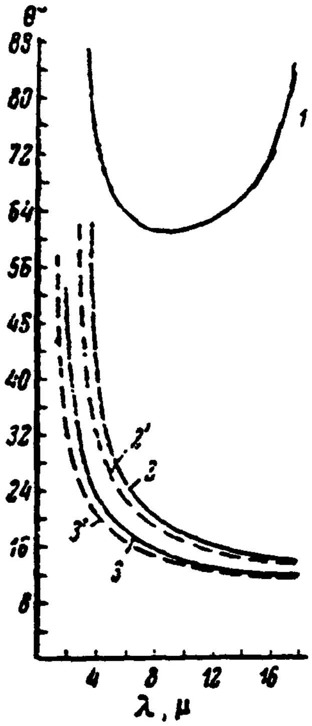
(Beregulin 1974) show phasematching angle versus infrared wavelength plots for IR pumped by Nd:YAG (1.06μm) or ruby (O.6943 μm). Figure 28. Next they treat the conversion of CO_2 laser radiation (l_1 = 10.6 μm) using Nd:YAG (l_2 = 1.06 μm) and obtain:

Type of interaction	Θ in degrees	d_{eff} X 10^{14} $n_1n_2n_3$ cgs
o + o = e	12.95	0.17
e + o = e	13.63	0.16
o + e = e	61.36	0.011

(Abdullaev 1975) performed a number of experiments where Nd:YAG laser light was mixed with CO or with CO_2 for down conversion. (Beregulin 1975) mixed λ_1 = 10.6μm and λ_2 = 1.15 μm for various thicknesses and orientations of GaSe. Comparison of the theoretical and experimental values is given in Table 4. Therein, the quantum efficiency $\eta = P_3\omega_1/P_1\omega_3$ where $P_i$is the radiation power and ω_i its frequency. η_m is the maximum value of the quantum efficiency which is a function of the pump power density, thickness of nonlinear crystal ℓ, and d_{jk}. θ is the angle between the optic axis and the direction of propagation of the wave. φ is the angle between the (01$\underline{1}$0) crystallographic plane and the principal plane of the crystal.

Table 4 Comparison of theory and experiment

Sample No.	l, cm	$\eta'_{ex}\cdot 10^4$, $W^{-1}\cdot cm^{-2}$	$\eta'_{th}\cdot 10^4$, $W^{-1}\cdot cm^{-2}$	θ_0^{ex}, deg	θ_0^{th}, deg	$\Delta\theta_{th}$, deg	$\Delta\theta_{ex}$, deg	φ_0^{ex}, deg	φ_0^{th}, deg
				$o+o=e$					
1	0.025	1.5	6.4	12.6	12.6	0.49	0.57	31$\pm$5	30
2	0.1	1.1	6.4	13.0	12.6	0.14	0.14	30$\pm$5	30
3	0.7	2.0	3.0	62.8	12.6	0.10	0.02	33$\pm$5	30
				$e+o=e$					
1	0.025	1.6	6.2	13.9	13.3	0.57	0.63	60$\pm$5	60
2	0.1	1.6	6.2	13.7	13.3	0.16	0.16	62$\pm$5	60
3	0.7	1.4	2.9	13.6	13.3	0.10	0.02	59$\pm$5	60



Dependence of the phase-matching angle θ on the infrared wavelength λ_1 in the case of pumping with λ_2 and different types of interaction: 1) o + e = e; 2, 3) e + o = e; 2', 3') o + o = e; λ_2 (μ): 1), 3, 3') 1.06; 2, 2') 0.6943.

Beregulin et al, Sov. Phys.- Semiconductors 8 122 (1974)

Figure 28 Dependence of the phase matching angle in GaSe upon various interacting infrared wavelengths

By taking the difference frequency of a ruby and tunable dye laser, (Abdullaev 1976) was able to generate 10-17 μm outputs.

(Bianchi 1978) down converted an OPO output pumped by a Nd:YAG to the 5-11 μm range, Figure 29. (Bianchi 1979) extended the work to cover the range of 4-18μm.

(Oudar 1979) mixed the output of a Nd:YAG laser and an infrared dye laser it was pumping to cover a tuning range of 9-19 μm. They show curves of phase matching angle versus wavelength for Type I and Type II configurations. (Kupecek 1979) continued these downconversion experiments using both Type 1 & 2 phasematching of GaSe in a difference frequency process yielding outputs from 9-19 μm.

(Abdullaev 1989) gives $d_{22} = 1.9 \pm 0.4 \times 10^{-7}$ cm/dyn$^{1/2}$. A better agreement between theory and experiment were obtained taking $d_{22} = 1.5 \times 10^{-7}$. They observed SHG for 9.3, 9.6, 10.3, and 10.6 μm.

(Vodopyanov 1991) had a system where they used an Er^{3+}:YAG laser at $\lambda = 2.94$ μm to pump either a GaSe or a $ZnGeP_2$ crystal. The output from the $ZnGeP_2$ covered the region from 3.5 - 9.3 μm and the GaSe from 4 - 18 μm. Angular tuning curves are shown in Figure 30.

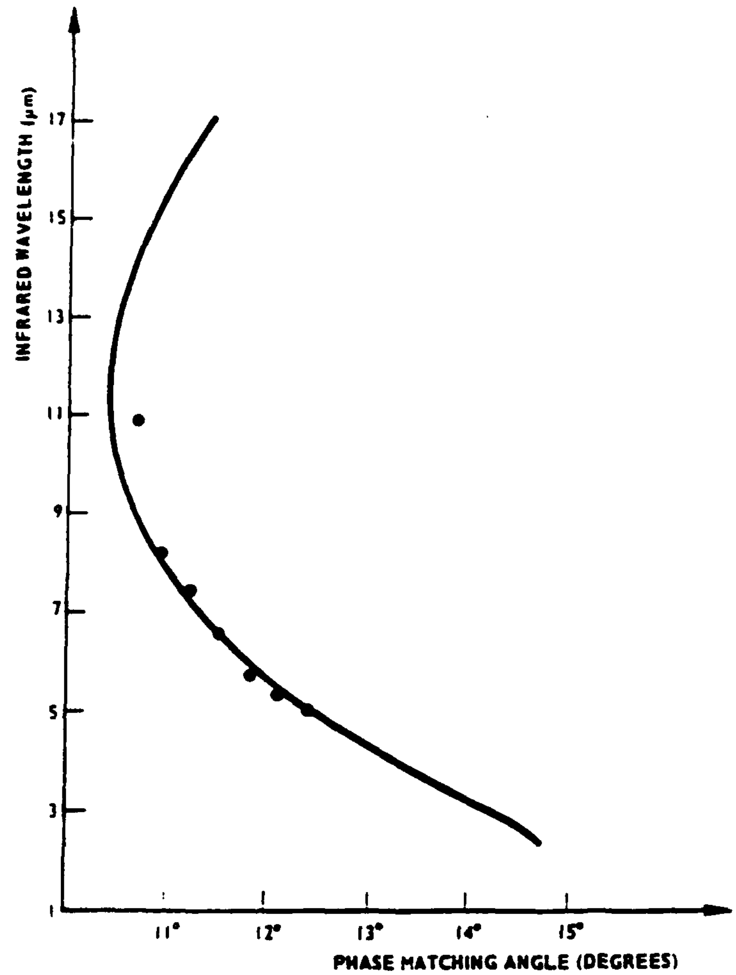
(Seilmeier 1991) reported generating picosecond light pulses from 4-18 μm using GaSe. The pulses were used to study GaAs/ $Al_xGa_{1-x}As$ multiple quantum structures by an infrared bleaching technique.

From 23 September- 3 October 1992, I visited several Institues of the Russian Academy of Sciences. One of these was the Institute of Atmospheric Optics near Tomsk, Siberia. While in Tomsk I had extensive talks with Dr. Yuri Andreev, one of the world's experts on nonlinear optics in the mid-infrared. He once headed a section of IAO but was then teaching in the Tomsk Medical Institute and affiliated with two companies, Vostok (East) and Amethyst. The follwing is taken from my trip report. "Next Andreev talked about GaSe. The biggest problem with the material is that it is soft. How to hold the material without deforming it remains to be solved. At 2 mm the absorption coefficient is 0.01 cm^{-1}. He has used a Nd pumped F_2 laser to generate difference frequencies up to 6-13 mm. Claims the crystal is not good for low power lasers. It is better for mid- to high-power lasers. Use a large aperture. With the large birefringence, it is easy to phase match. It can be pumped with 1.06 mm. The big question is damage. Kulevskii finds internal damage; Andreev finds surface damage. He also briefly mentioned that he could supply laser crystals, a 10?x6x100 mm Er:YSGG (2.94 mm) crystal for about $1000."

(Vodopyanov 1993) working at $\lambda = 3$ μm reports $d_{eff} = 54.4 \times 10^{-12}$ m/V. The corresponding figure of merit $d^2/n^3 = 127.8 \times 10^{-24}$ m^2/V^2. The optical parametric generator (OPG) threshold intensity, $I_{thr} = 6$ GW/cm^2. Tuning range achieved with a $\lambda = 2.79$ μm pump was 3.5 -18 μm.

(Laenen 1993) produced a 2.2 ps pulse at 7.2 μm using difference frequencies from a Nd:glass laser.

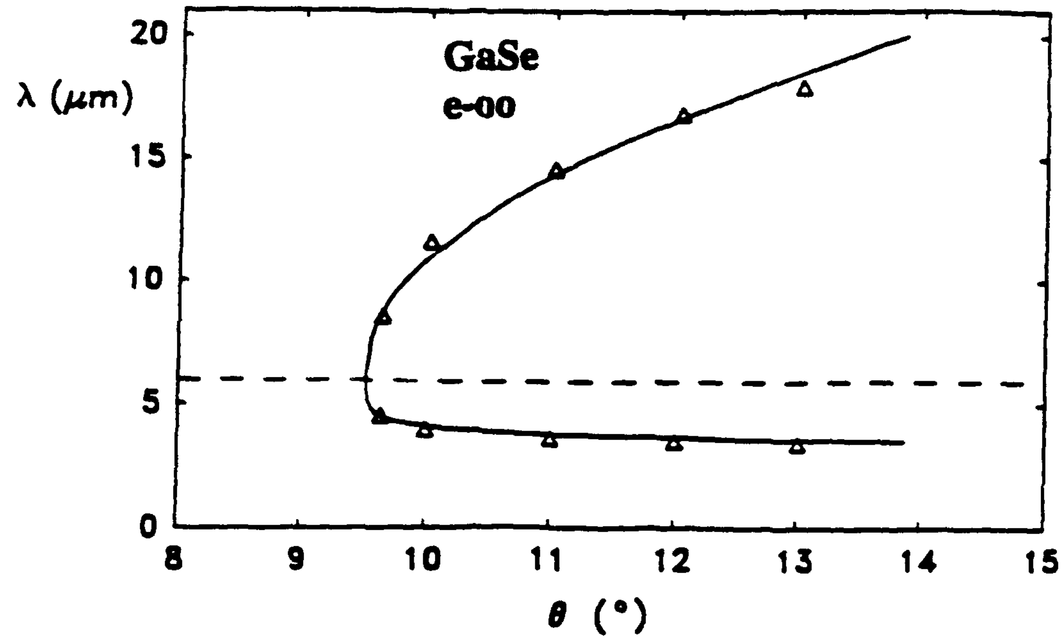
Another nonlinear effect, optical bistability, is treated in a paper by (Stadnik 1988).



Angular tuning curve for GaSe down-conversion. The continuous curve is calculated from the Sellmeier equations of ref. [4].

Bianchi et al, Optics Communications 25 256 (1978)

Figure 29 Angular tuning curve for GaSe down-conversion



Angular-tuning curves for a pump with $\lambda = 2.94$ μm. GaSe (type I); solid curve, calculated from data in Ref. 2.

Vodopyanov et el, Optics Communications **83** 322 (1991)
Vodopyanov, J. Opt. Soc. Am. B 10 1723 (1993)

Figure 30 Angular tuning curves for GaSe

5.10 **Multiphoton Excitation:**

Most of the work in this category concerns two-photon excitation. The majority of these effects occur around 590-600 nm. Papers concerning two-photon effects are: (Abdullaev 1971), (Adduci 1977), (Akhundov 1972), (Baltramiejunas 1991), (Cataleno 1977), (Kawarada 1974), and (LeToullec 1981). Papers concerned with higher multiphoton effects, mostly four-photon, are: (Catalano 1977), (Minami 1990), and (Petnikova 1988,1989).

6.0 CONCLUSIONS

GaSe is a leading candidate for nonlinear optical conversion devices in the mid- to far-infrared. This report summarizes the properties of the material and contains a bibliography which tries to list all the known papers on GaSe.

A capsule summary of properties of GaSe for nonlinear optical applications in the 10-18 μm wavelength range is as follows:

Good points:

- Broad transparency range - 0.65-18 μm
- Low absorption - less than 1 cm^{-1}
- Large nonlinearity- among top 5 in far infrared
- Large bifringence- easy to phase match
large acceptance angle
- Optically useful (001) faces from careful cleaving
- Large thermal conductivity $\perp$ optic axis
- Moderate laser damage but still better than most other far-ir materials

Weak points:

- Soft material - may sag with high average power useage
- Cannot polish nor cut for phase match angle
- Moderate melting temperature ~ 950^{o}C
- May have walk-off problems
- Moderate nonlinear threshold

APPENDIX

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